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PROCEEDINGS OF THE FIRST AND SECOND SYMPOSIA ON COMBUSTION

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Symposium (International) on
Combustion.

PROCEEDINGS
OF THE

First Symposium on Combustion

(Held at the Seventy-sixth Meeting of the American Chemical Society at
Swampscott, Massachusetts, September 10-14, 1928)

AND THE

Second Symposium on Combustion

(Held at the Ninety-fourth Meeting of the American Chemical Society at
Rochester, New York, September 9-10, 1937)



THE COMBUSTION INSTITUTE



Pittsburgh, Pennsylvania

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PREFACE TO VOLUMES I-II

The International Combustion Symposium Volumes have become a necessary part of the reference library of anyone working in the area of combustion, flames, and explosions. The question often asked is "Why is the Third Symposium volume the first?" With the issue of this volume, it no longer is.

In September 1928, the Gas and Fuel Division of the American Chemical Society sponsored a Symposium on Combustion, with Professor G. G. Brown as Chairman. The papers were presented as part of the annual American Chemical Society Meeting at Swampscott, Massachusetts, and in print occupied 60 pages in the journal, *Industrial and Engineering Chemistry*. In 1937, Dr. Bernard Lewis was instrumental in organizing a Second Symposium on Combustion, which was again sponsored by the American Chemical Society at its annual meeting in Rochester, New York. Dr. Lewis was Chairman. The papers were printed in three successive issues of *Chemical Reviews*.

The Second World War served to emphasize the practical significance of combustion research, particularly in the area of high-output combustion in aviation power plants; and at the instigation of Dr. Lewis a group of individuals met in Pittsburgh to consider the desirability of holding a Third Symposium on Combustion. This one, with Dr. Bernard Lewis and Professor J. O. Hirschfelder as Joint Chairmen, was held at the University of Wisconsin in August 1948. It was the first to devote a full week to combustion, the first not sponsored by an existing scientific or technical society, the first to which a large number of contributors and guests from outside the United States was invited, and the first to be published in a single volume. At the Wisconsin meetings a Standing Committee was set up to maintain continuity of the concept of more-or-less regular combustion symposia, and to handle finances. After the Fourth Symposium at Massachusetts Institute of Technology in 1952, and the Fifth at the University of Pittsburgh in 1954, The Combustion Institute was founded; and succeeding Symposia were held under the auspices of that new society.

The Third Symposium might justifiably, in the light of later developments, have been labeled First International Symposium, but it was not; and it now appears appropriate to claim Symposia I and II as part of the series. It is difficult for the young engineer or scientist to visualize the relatively primitive state of knowledge of

fluid mechanics and nonisothermal chemical kinetics, especially in application to combustion, in 1928 when the First Symposium on Combustion was held. Those of us who have worked in the combustion area for a long time are reminded, by reading the papers in this volume, of how far combustion has come as a field of science and engineering since then. At the same time we are impressed with the clear evidence that the basis was being laid, in those days, for today's powerful approach to problems considered wholly unmanageable in the 1930's. The Burke and Schumann paper on diffusion flames cut through the intricacies of the multi-component diffusion process and represented the first development of the concept of a material sink in a two-component diffusion process, with the solution for locus of the sink determining the position of the flame front. This paper had perhaps more influence on the engineering science of combustion than any ever published. The Smith and Pickering paper presaged the detailed studies, twenty years later, of cellular flame structure and the multizone structure of premixed flames. W. E. Garner's examination of flame-radiation data shows the effects of seeking chemical explanations of phenomena more dependent on thermal or fluid mechanical processes. Stevens' soap-bubble method of studying constant-pressure flame propagation in homogeneous mixtures produced data which have never been understood. Payman's useful empirical rules for converting flame-speed or pressure-rise data for one geometry to values applicable to another are recorded. The First Symposium closes with several papers on the then-pressing problem of engine knock.

The Second Symposium papers show the growth in sophistication of combustion research that characterized the nine-year period since the First. The papers by Brewer, Bradford and Finch, Landau, and Townend laid the basis for considering the ignition process quantitatively. The papers of Pease, of Harris and Egerton, of Newitt on hydrocarbon oxidation, the summary paper by von Elbe and Lewis on hydrocarbon combustion mechanism, Kassel's pioneering work on the first and second limits of hydrogen explosion are early contributions in a field which has grown explosively but still leaves unanswered many of the questions raised in 1937. The papers on flame propagation are headed by the paper of Lewis and von Elbe, one of the first to attempt quantitative testing of a mathematical model of flame propa-

gation against fundamental data. Several papers on combustion thermodynamics show how to handle problems of the burned gas in open flames and engines. A large number of papers on Diesel and Otto cycle engines attest to the pressing problems of knock in engines. The Lovell and Campbell paper on the relation of molecular structure of fuels to their tendency to knock in an Otto cycle engine is the first paper in a distinguished series which brought order into the area

and gave us a quantitative empirical picture of structure in relation to knock; but we do not even today have the full explanation of their orderly findings.

The First and Second Symposium papers well deserve to join the later volumes of this distinguished series.

H. C. HOTTEL

Cambridge, Massachusetts
July 1964

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PROCEEDINGS OF THE FIRST AND SECOND SYMPOSIA ON COMBUSTION

First Symposium on Combustion

INTRODUCTION

GEORGE GRANGER BROWN, Chairman

University of Michigan, Ann Arbor, Michigan

Combustion is without exaggeration the most important reaction to the human race. All human and animal existence depends upon combustion as its source of energy. The first real progress man made in his ascent or descent from the anthropomorphic missing link depended upon his control of fire or combustion; and in many ways our further progress depends upon more intelligent and efficient control of combustion.

Originally used to create a flickering light and worshipped as the "Fire God," further experience and knowledge led to more efficient uses for combustion as a source of heat, and relatively recently as a source power in the internal-combustion engine. Although the flickering luminous flame has been known since long before "Hector was a pup," we are still studying these "simple" diffusion flames, and apparently the first adequate mathematical treatment is presented in this symposium. The "flicker" and temperature of, and radiation from, flames, as well as some unusual structures of Bunsen flames which may tend to reestablish the worship of the "Fire God," are also representative of further progress in our study of stationary flames.

Since Berthelot and LeChatelier discovered the detonation wave and developed a photographic method for studying the propagation of flame through explosive or inflammable mixtures, the study of flame propagation has been steadily increasing in popularity. Like most such intensive studies, "the more we work the more work we find to do." The five papers dealing with flame propagation not only indicate the relations existing between the rate of flame propagation, rate of chemical action, physical properties of the mixture and pressure propagation, but also raise new questions to be answered only by further work.

These studies of flame propagation are closely allied with the use of combustion as a direct source of power. Internal-combustion engines are used because of their high efficiency and convenience as the source of power for all kinds of transportation—vessels, submarines, railroads, mines, automobiles—but are absolutely essential only for airplanes or dirigibles. The lifting ability of a plane depends upon its velocity through the air, which in turn depends upon the power of the motor. Until the internal-combustion engine was available with its low weight per horsepower, the weight of the power plant always exceeded the lifting capacity of the plane. Just as the internal-combustion engine made possible the airplane, so is further development of the airplane dependent upon still lower weights per unit of power. The efficiency of present plane and propeller design is so high that there is little opportunity for improvement along these lines. But if the weight of the motor and fuel could be reduced, or its power proportionately increased, so much more "pay load" could be carried. The one practical way to reduce the weight of the motor or to increase its power and efficiency is to increase its compression ratio. This compression, or expansion, ratio is limited by that peculiar form of combustion known as engine knock or detonation. A large part of this symposium is devoted to papers on the mechanism of combustion and autoignition temperatures of fuels in an attempt to find the true cause of engine detonation, the importance of which can hardly be overemphasized.

The chairman wishes to thank the officers of the Divisions of Gas and Fuel Chemistry and Petroleum Chemistry and authors of the many excellent papers for the splendid cooperation without which this symposium would not be possible.

DIFFUSION FLAMES

S. P. BURKE AND T. E. W. SCHUMANN

Combustion Utilities Corporation, Linden, N. J.

In general, flames may be divided into two classes: flames of the Bunsen type in which the combustible gas and air are premixed before ignition occurs and flames in which the combustible gas and air meet coincidentally with the occurrence of combustion. To this second class of flames the authors have applied the term "diffusion flames."

An analysis of this type of flame has been made which has led to a theory of its mechanism. A mathematical presentation of the theory is given and also the results of an extensive experimental investigation of the deductions therefrom. As a consequence of this work considerable light is shed on the physical characteristics, the mechanism, and the general properties of this very common class of flames.

Whenever two gas streams, one a combustible gas and the other a gas capable of supporting combustion, impinge or meet under conditions such that combustion occurs, a surface of flame will be produced. It is to flames of this character as distinguished from flames produced in a mixture of oxygen and a combustible gas that we have given the name "diffusion flames." The flame of a match, of a candle, and of the familiar gas-jet burner are all of this type, and it will be readily appreciated that this class of flames is not uncommon.

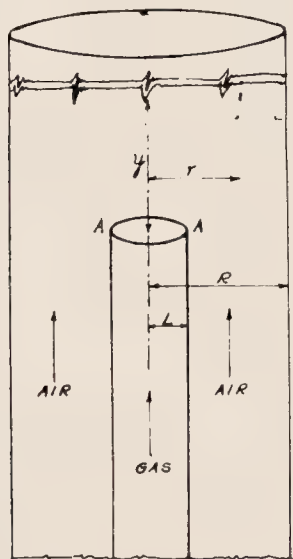


FIG. 1. Diagram of experimental burner.

Many investigations have been made on the Bunsen type flame; an adequate theory has been advanced to account for the shape and general properties of the characteristic Bunsen cone, and the mechanism of combustion in this case is fairly well understood. Diffusion flames, on the other hand, have received but scant attention. A comprehensive search of the literature did not reveal a single attempt to account for the shapes and properties of diffusion flames, except in a general descriptive way.

A typical flame of the class with which we are concerned can be produced readily in the apparatus shown in Fig. 1, the essential part of which consists of two concentric tubes. Combustible gas flows upward through the inner tube of radius L , and at the opening AA comes in contact with the air which flows through the outer tube of radius R . Any radial distance is represented by r , and y is any vertical distance measured from AA . The rate of flow of gas to that of air, as measured by flowmeters, is kept in the ratio L^2 to $R^2 + L^2$, which means that the velocity of the gas is maintained the same as the velocity of the air. If the gas is ignited at AA , it will, under proper conditions, burn with a steady flame of definite shape.

Flames produced in this manner in cylindrical tubes are called cylindrical flames. Flat flames are produced when the cylindrical tubes are replaced by parallel plane surfaces. In this case the combustible gas flows between the two inner, and the air between the two outer, walls. If $2L$ is the distance between the two outer walls, and if the velocities of gas and air are to be identical, the rate of flow of gas compared with that of the air must have the ratio of L to $R - L$.

Proposed Theory

If the problem of determining the physical characteristics of these flames is to permit of mathematical treatment certain fundamental assumptions must be made. Let us therefore assume that (a) the velocity of the gas and air up the tube in the region of the flame is constant; (b) the coefficient of interdiffusion of the two gas streams is constant; (c) the interdiffusion is wholly radical; and (d) admixture of the two gas streams occurs by diffusion only.

At first these assumptions seem to be improbable. Thus, owing to the high temperature developed by the flame and the consequent expansion of the gases, there will certainly be large differences in velocity at different points on the vertical axis of the tube. On the other hand, owing to these temperature variations the co-

efficient of interdiffusion would be expected to vary. It is to be noted, however, that any increase in velocity due to rise in temperature tends to be counterbalanced by a corresponding increase in the diffusion in so far as its effect on the size and shape of the flame is concerned. Assumptions (a) and (b) when taken in conjunction may therefore be advanced as heuristic and possibly as legitimate. Assumption (c) will be valid only for fairly tall flames. For short flames the axial diffusion would play an important part, but the mathematical treatment remains essentially the same.

For the present let us confine ourselves to tall flames and neglect axial diffusion. Since we are concerned with steady flames and are thus forced to postulate stream-line flow, it is evident that the only combustion that can take place is due to the interdiffusion of oxygen and the combustible gas. Combustion is therefore considered to be confined to a surface, called the flame front, where oxygen and combustible gas meet to combine and form the neutral products of complete combustion. Experiment confirms this statement, since in all flames of this type there is a very distinct flame front, the thickness of which in most cases is so small that it may be treated as a geometrical surface. With this fact in mind it is logical to define the flame front as "the locus of those points where the rate of diffusion of combustible gas outward and the rate of diffusion of oxygen inward have the ratio required by the stoichiometrical equation for complete combustion of the combustible gas."

Having defined the problem, we may now proceed to its solution, and for this purpose the following symbols will be employed:

- v = velocity of gas or air (assumed constant)
- R = radius of outer tube
- L = radius of inner tube
- r = radial distance
- x = radial distance of flame front
- y = vertical distance above orifice of inner tube
- k = coefficient of interdiffusion
- C_1 = initial concentration (partial pressure) of combustible gas
- C_2 = initial concentration (partial pressure) of oxygen
- C = concentration of combustible gas at any point
- $C_0 = C_1 + C_2/i$
- t = time
- i = number of molecules of oxygen which combine with one molecule of combustible gas to effect complete combustion

In the mathematical analysis we have to solve the equation of diffusion for the gas and for the

oxygen, subject to certain boundary and initial conditions, and also subject to the condition that at the flame front the molecules of gas and oxygen combine to form neutral products of combustion. But the flame front is not yet determined, so that one of the boundary conditions is indeterminate. This difficulty, however, can be easily overcome by the following simple device: Since the oxygen combines with the gas to form a neutral product, for purposes of mathematical analysis the oxygen may be regarded as negative combustible gas. Thus a concentration C_2 of oxygen will be equivalent to a concentration $-C_2/i$ of gas. In this case, therefore, we have positive gas diffusing into negative gas and the flame front will be the surface where the concentration of combustible gas is zero. Our problem thus reduces to one of diffusion of a single gas having a certain initial distribution and subject to certain boundary conditions.

The equation of diffusion is

$$\frac{\delta C}{\delta t} = k \left(\frac{\delta^2 C}{\delta r^2} + \frac{1}{r} \frac{\delta C}{\delta r} \right)$$

but since we have assumed a constant velocity v , $y = vt$. Hence

$$\frac{\delta C}{\delta y} = \frac{k}{v} \left(\frac{\delta^2 C}{\delta r^2} + \frac{1}{r} \frac{\delta C}{\delta r} \right) \quad (1)$$

The initial concentration is

$$C = C_1 \text{ from } r = 0 \text{ to } r = L \text{ at } y = 0$$

$$C = -C_2/i \text{ from } r = L \text{ to } r = R \text{ at } y = 0$$

and the boundary conditions are $\delta C/\delta r = 0$ when $r = 0$ and when $r = R$. The solution of Eq. (1) which satisfies the given conditions is

$$C = C_0 \frac{L^2}{R^2} - \frac{C_2}{i} + \frac{2LC_0}{R^2} \sum \frac{1}{\mu} \frac{J_1(\mu L) J_0(\mu r)}{(J_0(\mu R))^2} \times \exp[-k\mu^2 y/v] \quad (2)$$

where μ assumes the value of all the positive roots of the equation, $J_1(\mu R) = 0$, and J_1 and J_0 are Bessel's functions of the first kind.

The equation for the flame front is obtained by putting $C = 0$ and $r = x$, whence

$$\begin{aligned} \sum \mu^{-1} \frac{J_1(\mu L) J_0(\mu x)}{(J_0(\mu R))^2} \exp[-k\mu^2 y/v] \\ = \frac{R^2 C_2}{2LiC_0} - \frac{1}{2}L = E \text{ (say)}. \end{aligned} \quad (3)$$

The shape of the flame front will be given by the values of x and y which satisfy this equation.

The height of the flame is given by the value of y in Eq. (3) when (a) $x = R$ for an under-

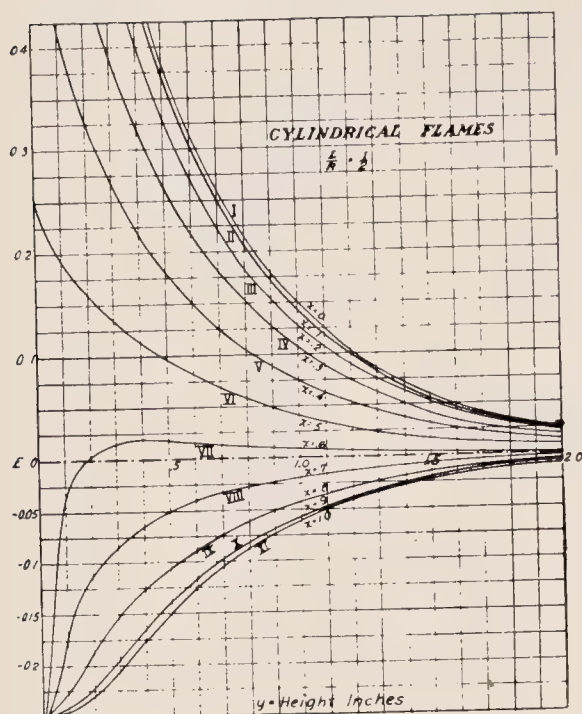


FIG. 2. Curves showing relation between E and y when $L/R = \frac{1}{2}$.

ventilated flame, and (b) $x = 0$ for an over-ventilated flame.

It is obvious that in an overventilated flame O_2 is in excess and consequently the flame surface will terminate at the axis of the tube—that is, at $x = 0$. Similarly, the flame surface of an under-ventilated flame will terminate at $x = R$.

Our procedure to determine the shape of any given flame where R and L are known will be to plot the value of E against y for a set of values of x ranging from 0 to R . Such a set of curves is shown in Fig. 2. In drawing these curves it was assumed that

$$L = \frac{1}{2} \text{ inch}$$

$$R = 1 \text{ inch}$$

$$k = 0.0763 \text{ square inch per second}$$

$$v = 0.610 \text{ inch per second which corresponds to a flow of 1 cubic foot per hour in the inner tube}$$

The value adopted for k is the diffusivity of methane, which was the gas generally used in our experimental work. The method of employing the curves of Fig. 2 may be best illustrated by means of an example:

Suppose that the combustible gas employed is methane, the concentration of which we take to be unity, and that air is used in the outer tube; then

$$C_1 = 1$$

$$C_2 = 0.21$$

$$C_0 = C_1 + C_2/i = 1.105$$

$$i = 2$$

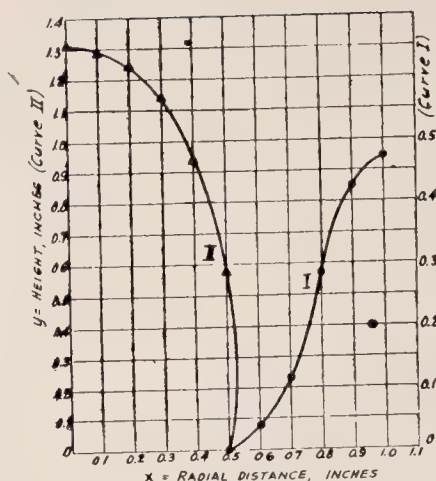


FIG. 3. Curve I, underventilated cylindrical flame; Curve II, overventilated cylindrical flame.

since $CH_4 + 2O_2 = CO_2 + 2H_2O$ is the stoichiometrical equation. From Eq. (3)

$$E = R^2 C_2 / 2LiC_0 - L/2 = -0.155$$

From the curves in Fig. 2 corresponding to this value of E , we find a set of values of x and y .

$x = 1.0$	0.9	0.8	0.7	0.6
$y = 0.47$	0.43	0.29	0.11	0.04

If pure oxygen were used instead of air, then $C_2 = 1$, and $C_0 = C_1 + C_2/2 = 1.5$, and $E = 0.083$.

From Fig. 2 we find the values of x and y for this value of E thus:

$x = 0$	0.1	0.2	0.3	0.4	0.5
$y = 1.31$	1.29	1.24	1.14	0.94	0.58

The results of the above calculations are shown graphically in Fig. 3. Curve I shows the shape of the underventilated flame where the outer tube contained air, and Curve II, that of the over-ventilated flame where oxygen was substituted for air. The vertical scale of Curve I is double that of Curve II. Our experimental results will subsequently be compared with these theoretical curves.

Flat Flames

Using the same notation as before and assuming that the combustible gas flows through a duct bounded by two parallel walls whose distance apart is $2L$, and that the air flows in an outer duct whose width is $2R$, we have the equation of diffusion

$$\frac{\delta C}{\delta y} = \frac{k}{v} \frac{\delta^2 C}{\delta r^2}.$$

The solution of this equation fitting the boundary conditions is

$$C = C_0 \frac{L}{R} - \frac{C_2}{i} + \frac{2C_0}{\pi} \sum \frac{1}{n} \sin \frac{n\pi L}{R} \cos \frac{n\pi r}{R} \times \exp (-kn^2\pi^2 y/vR^2]. \quad (4)$$

Putting $C = 0$ and $r = x$, we have the equation for the flame front

$$\sum_1^\infty \frac{1}{n} \sin \frac{n\pi L}{R} \cos \frac{n\pi x}{R} \exp [-kn^2\pi^2 y/vR^2] = \frac{1}{2}\pi \left\{ \frac{C_2}{iC_0} - \frac{L}{R} \right\} = E. \quad (5)$$

Again, let us consider a particular case. Suppose

- $R = 1$ inch
- $L = \frac{1}{6}$ inch
- $k = 0.0763$ square inch per second
- $C_1 = 1$
- $C_2 = 0.21$
- $i = 2$
- $v = 1.33$ inch per second.

This value of v is taken simply for convenience of computation since, as will be shown later, the

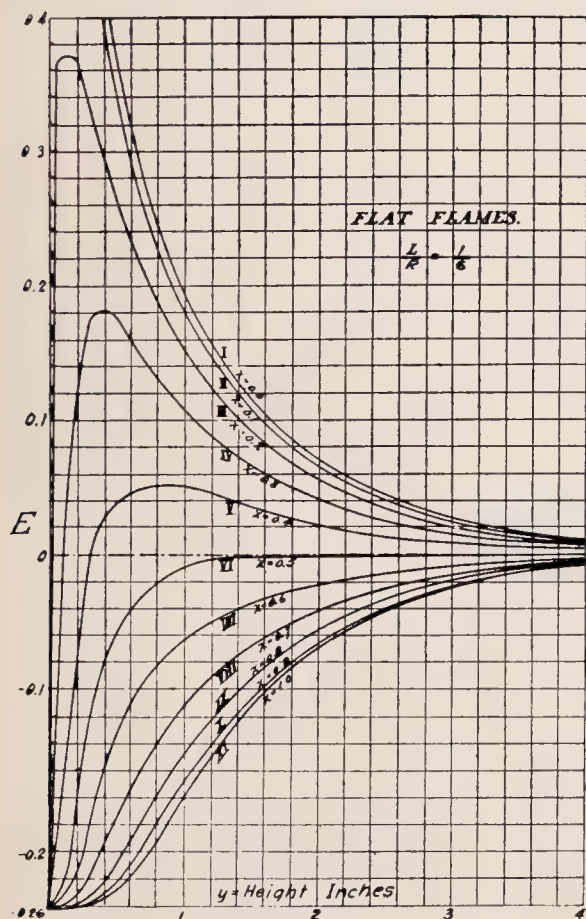


FIG. 4 E and y curves for flat flames when $L/R = \frac{1}{6}$.

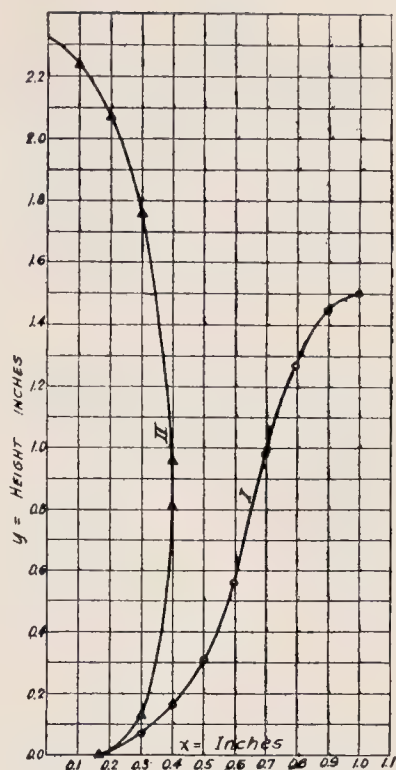


FIG. 5. Curve I, underventilated flat flame; Curve II, overventilated flat flame.

vertical dimension of any flame is directly proportional to v , and it is thus of little significance what particular value we assign to v .

Now

$$E = \frac{1}{2}\pi \left(\frac{C_2}{iC_0} - \frac{L}{R} \right) = -0.113.$$

If enriched air containing 50 per cent oxygen is substituted for ordinary air, then $C_2 = 0.5$ and $E = 0.052$. Figure 4 shows a set of curves for flat flames corresponding to those given in Fig. 2 for cylindrical flames. If from these curves we read off the values of x and y corresponding to the above values for E , we find, when $E = -0.113$,

$x = 1.0$	0.9	0.8	0.7	0.6	0.5	0.4	0.3
$y = 1.50$	1.45	1.27	0.98	0.57	0.32	0.17	0.05

and when $E = 0.052$

$x = 0$	0.1	0.2	0.3	0.4
$y = 2.32$	2.24	2.07	and 1.76	and 0.96
		0.02	0.13	0.80

Curve I, Fig. 5, represents the shape of the underventilated and Curve II that of the overventilated flame.

Experimental

In Fig. 6 the photographs of some typical flames are reproduced, and Table I gives the data concerning them.

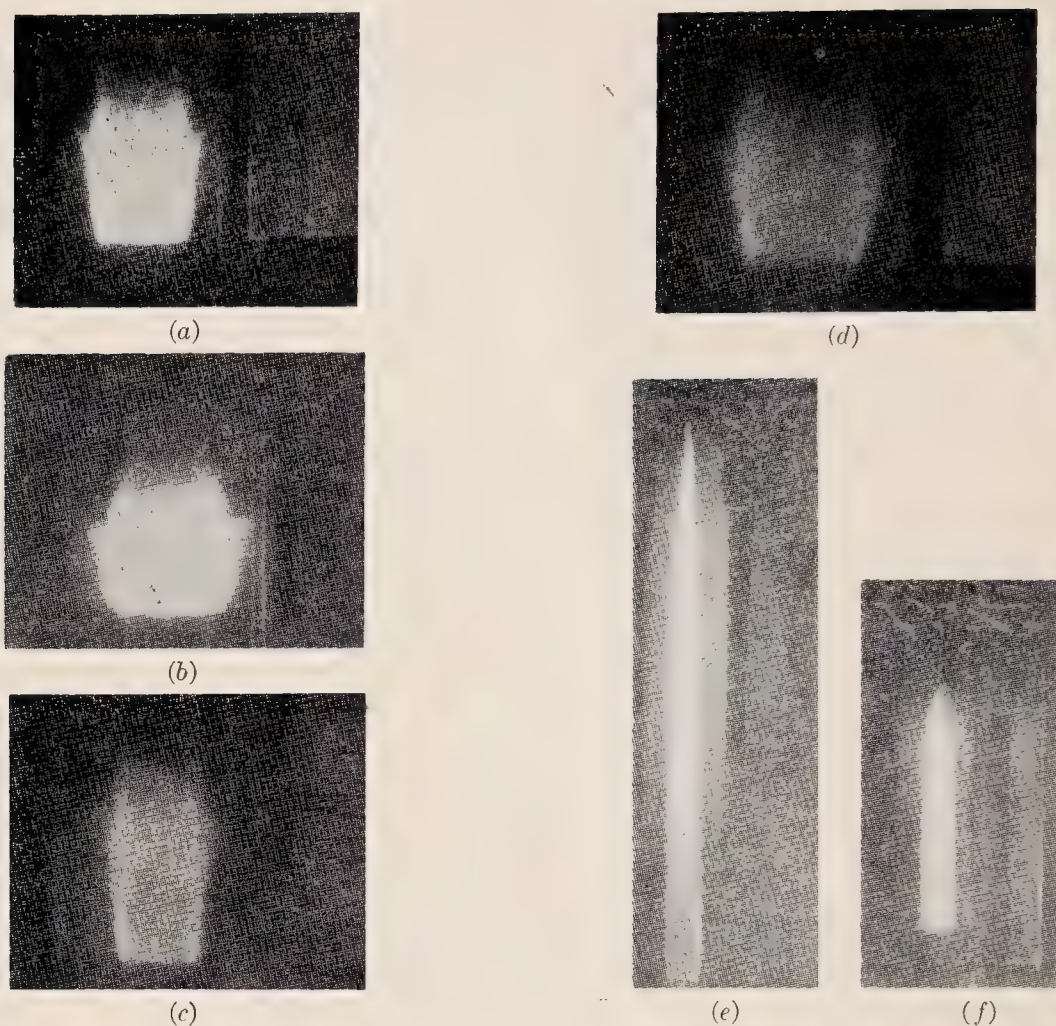


FIG. 6. Photographs of some typical diffusion flames.

Figures 6(a) to 6(d) represent underventilated flames. The flame front can be clearly seen to curve out towards the outer tube. The central bright part, which rises above the actual flame and gradually fades away, is due to incandescent carbon rising from the flame and has nothing to do with the actual flame front. Comparison of these flames with Curve I, Fig. 3, shows the general agreement between the actual and theoretical flame front. Figures 6(e) and 6(f) are

the photographs of overventilated flames, and again we notice a general agreement between their shapes and Curve II, Fig. 3, which represents the theoretical flame front of an overventilated flame. In a general way there is therefore agreement between theory and experiment.

Now it is possible to draw certain general conclusions from the theory concerning the heights of flames and in this way to test the theory by comparison with experiment.

TABLE I

Photo-graph	R , inch	L , inch	h , inches	Air, cu ft/hr	Methane, cu ft/hr	City gas, cu ft/hr	Nitrogen, cu ft/hr
6 (a)	$\frac{5}{8}$	$\frac{1}{4}$	0.87	6	2		
6 (b)	$\frac{5}{8}$	$\frac{1}{4}$	0.57	4		2	
6 (c)	$\frac{3}{8}$	$\frac{3}{16}$	0.88	6	2		
6 (d)	$\frac{5}{8}$	$\frac{5}{16}$	0.84	6	2		
6 (e)	$\frac{1}{2}$	$\frac{3}{16}$	8.1	32	2		
6 (f)	$\frac{1}{2}$	$\frac{3}{16}$	3.5	32	1		1

Effect of Varying Dimensions of Tubes. If in Eq. (3), which is the mathematical expression for the shape of the flame front, we multiply R , L , and x by the common factor M , keeping the total flow constant so that v has $1/M^2$ its original value, then the equation remains unaltered, since μ assumes $1/M$ of its former value. From this we infer that the height of any cylindrical flame is not affected by the size of the tubes if the flow of gas and of air are kept constant. Figures 6(c) and 6(d) illustrate this, for the table shows that the heights of the flames are practically the same in both cases.

Effect of Variation in Coefficient of Diffusion. In Eq. (3), if k is multiplied by a factor M , y must be multiplied by $1/M$ to keep the equation unaltered. The height of a flame is therefore inversely proportional to the coefficient of diffusion, provided the other factors do not change. Two gases which can be compared conveniently are carbon monoxide and hydrogen, since their stoichiometrical equations for complete combustion are similar. Table II contains the data of experiments performed to illustrate this point.

The ratio of the height of the carbon monoxide flame to that of the hydrogen flame is 2.5, whereas the ratio of the coefficient of diffusion of hydrogen to that of carbon monoxide at room temperature is approximately 4. From this it would appear that the results are not strictly in accord with the theory, but it is not to be expected that the coefficients of diffusion as measured at room temperature will apply strictly to calculations on the shapes and sizes of flames.

Effect of Addition of Inert Gas to Combustible Gas. The substitution of an inert gas such as nitrogen for part of the combustible gas, while maintaining the total flow in the inner tube constant, results in a decrease in the value of C_1 . From Eq. (3) we see that a decrease in the value of C_1 or C_0 causes an increase in the value of E . Now, the height of an overventilated flame is given by Curve I, Fig. 2, and it is clear that any increase in E will mean a decrease in the height of the flame. On the other hand, Curve XI, Fig. 2, gives the height of an underventilated flame,

TABLE II

R , in.	L , in.	Air cu ft/hr	Carbon monoxide cu ft/hr	Height of flame (h), in.
0.63	0.42	22.2	25	2.75
0.63	0.42	22.2	25	6.95

TABLE III

Air, cu ft	Methane, cu ft	Height of flame (h), in.	Height of flame Cu. ft. CH ₄
7.0	0.38	1.23	4.56
13.5	0.75	3.37	4.50
18.0	1.00	4.47	4.47
23.8	1.32	5.82	4.40
29.5	1.64	7.25	4.42
37.1	2.06	9.00	4.36
41.1	2.28	9.90	4.32

and here an increase in E produces an increase in the height.

In brief, substitution of inert gas produces an inward displacement of the flame front resulting in taller underventilated and shorter overventilated flames. That this is the case can be clearly seen by comparing Fig. 6(e) and 6(f), which are photographs of overventilated flames obtained under identical conditions, except that in the second case nitrogen was substituted for half of the methane, whereby the height of the flame was reduced from 8.1 to 3.5 inches. Theoretical calculations indicate that the flame with nitrogen should have been reduced to approximately half of its previous value. The agreement is seen to be good. Similarly, photographs of underventilated flames indicate that the substitution of nitrogen causes an elongation of the flame in all cases.

Effect of Variation in Flow. In Eq. (3) if v is multiplied by a factor, M , then the equation remains unaltered if y is multiplied by the same factor. It follows, therefore, that the vertical dimensions of a flame are directly proportional to the velocity of flow. Numerous experiments confirm this deduction. We quote one set of results obtained for overventilated flames (Table III). Similar results could readily be given for underventilated flames.

The ratio of the height of the flame to the velocity of flow is seen to be practically constant.

Effect of a Change in i (where i is the number of moles of oxygen combining with one mole of combustible gas). From Eq. (3) it is evident that an increase in i results in a decrease in the value of E , and as we have seen above, a decrease in E will cause an outward displacement of the flame front. Hence an increase in the value of i will result in taller overventilated and shorter underventilated flames. Table IV contains the results

TABLE IV

Expt.	<i>R</i> , in.	<i>L</i> , in.	<i>h</i> , in.	Air	City gas	Meth- ane	Eth- ane	<i>i</i>
1	$\frac{5}{8}$	$\frac{1}{4}$	1.44	6	2			1.05
2	$\frac{5}{8}$	$\frac{1}{4}$	0.87	6		2		2.0
3	$\frac{5}{8}$	$\frac{1}{4}$	0.62	6			2	3.5

of three experiments performed to prove this conclusion.

It is seen that there is a progressive decrease in the height of the flame which was underventilated, with an increasing value of *i*. Here again it is possible to show that there is not only a qualitative but also a quantitative agreement of experiment with theory: the value of *E* in each case is calculated from Eq. (3), and by means of Curve XI, Fig. 2, the theoretical height of the flame can be computed. Strictly speaking, the radius of the outer tube should have been exactly double the radius of the inner tube—i.e., *R* should have been $\frac{1}{2}$ inch instead of $\frac{5}{8}$ inch, but the fact that the outer tube was a little too large does not affect the result very much.

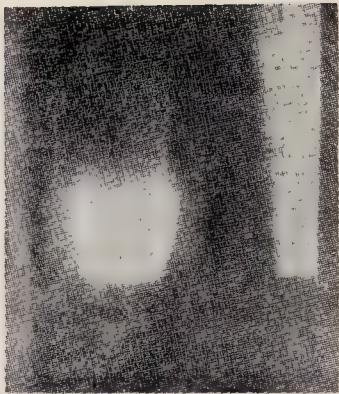
The city gas had a heating value of approximately 530 B.t.u. per cubic foot, which gives a value of *i* approximately equal to 1.05. Table V contains the calculated and experimental heights of the flames in the three cases.

The discrepancy between the calculated and experimental values in this table is to be attributed to the variations in diffusion coefficient of the three gases. This is especially true of the city gas, which contained a large per cent of hydrogen, tending to shorten the flame.

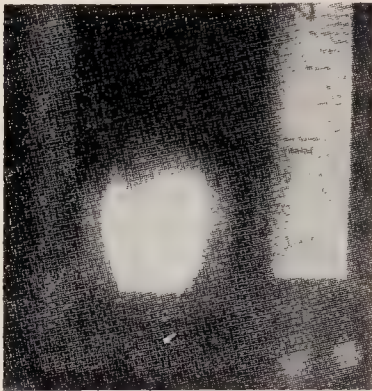
Effect of Variation in Pressure. Since the coefficient of diffusion of a gas is inversely proportional to the pressure, and since *v* is also inversely proportional to the pressure provided the total flow measured under standard conditions is kept constant, it is obvious that Eq. (3) will be unaffected by a change in pressure. The height of a

TABLE V

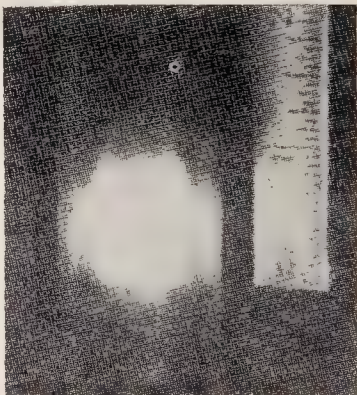
Expt.	Gas	<i>i</i>	<i>E</i>	<i>h</i> <i>h</i> (calc.), in. (exptl.), in.	<i>h</i> in.
1	City gas	1.05	−0.083	1.66	1.44
2	Methane	2.0	−0.155	0.93	0.87
3	Ethane	3.5	−0.194	0.67	0.62



(a) Atmospheric pressure



(b) Pressure, 3/2 atmospheres



(c) Preheat at 510°C.



(d) Preheat at 370°C.

FIG. 7. Photographs of flames showing effect of pressure and preheat.

flame would therefore be independent of pressure if all other factors are kept constant. This is borne out by experiment.

In Fig. 7(a) and (b), $R = \frac{1}{2}$ inch, $L = \frac{3}{16}$ inch, air = 4 cubic feet per hour, and $\text{CH}_4 = 2$ cubic feet per hour, the gases being measured under standard conditions. However, the pressure employed for Fig. 7(a) was 1 atmosphere while that of Fig. 7(b) was 1.5 atmospheres. The size and shape of these two flames by careful measurement are practically identical.

Effect of Preheating Gas and Air. The effect of increased velocity due to the heat developed in the flame has been assumed to be offset by a corresponding increase in the coefficient of diffusion (see theoretical assumptions). If this were true, then it would be logical to assume that preheating the gas and air should increase both the velocity of flow and the coefficient of diffusion, but in such a way that the effect of the one would neutralize that of the other with the result that the flame dimensions would not be altered.

Several experiments were performed in which an electric furnace about 14 inches long was placed around the outer tube of Fig. 1. In this way the gases passing through the concentric tubes were preheated. The results obtained are shown in Fig. 7(c) and (d) which should be compared with Fig. 7(a). Table VI presents the data. The temperatures shown are those recorded by a thermocouple placed alongside of the outer tube in the furnace. The actual temperature of the gases was of course considerably lower.

It would thus appear that preheating may have some slight effect on the height of the flame, but more experiments will have to be performed to determine accurately the magnitude of this effect.

Effect of Addition of Primary Oxygen to Combustible Gas. Substitution of oxygen for part of the combustible gas in the inner tube will decrease the value of C_1 and of E in Eq. (3); the flame front will be displaced inward and the effect will be similar to the case where an inert gas is added. We have, however, to distinguish two cases: (a)

where the addition of oxygen is so slight that combustion is confined to the flame front; (b) where sufficient oxygen is added for combustion to take place in the gas stream with the consequent formation of a Bunsen cone. In the second case the shape and size of the flame will not conform to Eq. (3).

That the flame front is displaced inward by the addition of oxygen to the combustible gas was confirmed by experiment.

Effect of Variation of Width of Ducts in Case of Flat Flames. Equation (5) gives the shape of the flame front of a flat flame. If in this equation R and L are multiplied by the common factor M , and the gas flows are kept constant, then the velocity v will be reduced to v/M , and x and y will both have to be multiplied by M to keep the equation unaltered. From this it follows that the height of the flame will be increased M times. It will be recalled that in cylindrical flames a variation in the dimensions of the tubes had no effect on the height of the flame so long as the flow remained constant. Except for this difference between flat and cylindrical flames, the previous discussions concerning the influence of temperature, pressure, addition of inert gas, etc., on cylindrical flames also hold good for flat flames.

Experiments were performed on flat methane flames, and the height of a particular flame was found to be 0.9 inch. When the size of the ducts was doubled the height of the flame as measured on the photograph was 1.6 inches. The photographs, however, were very indistinct, so that accurate measurement was impossible. The above result should therefore be regarded as a qualitative proof of the theoretical deduction that the height of a flat flame is directly proportional to the width of the ducts.

The experimental evidence produced above gives us confidence that our assumptions concerning the mechanism of diffusion flames are fundamentally correct, since all the deductions made from the theory have been verified by experiment. There still remains, however, a very potent method of testing the theory—namely, the chemical analysis of the products of combustion at different points in the flame.

Chemical Analysis of Gases in Diffusion Flames

In calculating the size and shape of any flame it is necessary to know the coefficient of diffusion of the combustible gas, but this coefficient as measured at atmospheric temperatures does not give proper results when applied in these flame calculations. It is therefore necessary to find the coefficient of diffusion which applies to flames.

TABLE VI

Figure	R , in.	L , in.	Flame height, in.	Air cu ft/hr	Methane cu ft/hr	Temperature °C
7 (a)	$\frac{1}{2}$	$\frac{3}{16}$	0.78	4	2	20
7 (c)	$\frac{1}{2}$	$\frac{3}{16}$	0.69	4	2	370
7 (d)	$\frac{1}{2}$	$\frac{3}{16}$	0.70	4	2	510

This was done in the case of methane by assuming a value for the coefficient which gave the best agreement with a particular experiment, and the value thus found was used for all further calculations on methane flames.

It is also possible, however, to use a different method for determining the coefficient of diffusion. By careful chemical analysis the constitution of the gas at different points along the axis of the concentric tubes can be determined and curves drawn showing the content of carbon dioxide, nitrogen, etc., against height. A value of the coefficient of diffusion is now selected which, when employed in the theoretical calculation of the same curves of composition *vs.* distance along the *y* axis (Fig. 1), will make the theoretical and experimental curves agree as closely as possible. The value of the coefficient so determined is now adopted as applying to the combustible gas in question.

The remarkable agreement of the size and shape of flames as calculated, employing a diffusion coefficient based on chemical analysis in the manner just described, with the photographic measurements of all flames from the particular gas, affords strong support to our theory of diffusion flames. An illustration of this procedure for the case of carbon monoxide flames is given by the following series of experiments.

- Flow of carbon monoxide = 4 cubic feet per hour
- Flow of air = 5.55 cubic feet per hour
- $R = 0.631$ inch
- $L = 0.408$ inch
- $L/R = 0.645$
- The carbon monoxide contained 3.2 per cent nitrogen.

TABLE VII

<i>y</i> , in.	N ₂ per cent	CO ₂ per cent	CO per cent	O ₂ per cent
0.25	3.8	0.0	95.8	0.4
1.04	23.0	11.2	62.8	0.2
1.75	41.0	20.3	38.6	0.2
2.63	48.4	25.1	25.6	0.2
3.75	50.9	26.9	21.9	0.0

A small water-cooled sampling tube was introduced vertically into the flame and small samples of gas were withdrawn from different points on the axis of the tube. The samples were taken at such a rate that the shape of the flame and the conditions of flow were not affected. Duplicate determinations were made in every case. The results of the analysis are given in Table VII.

In Fig. 8 these results are shown graphically, together with the curves which were calculated theoretically on the assumption that the coefficient of diffusion for CO = 0.104 square inch per second. The agreement between the theoretical curves and the experimental points is evident.

The method of calculating the concentrations of the various constituents yielding the theoretical curves shown on Fig. 8, while complicated and laborious, is sufficiently straightforward to require no detailed description. The procedure adopted was to consider the interdiffusion of the two gases to take place as though no flame were present. The mixture of gas so calculated for any given point was then assumed to react and the products thus obtained gave the final calculated analysis at the point in question. From chemical

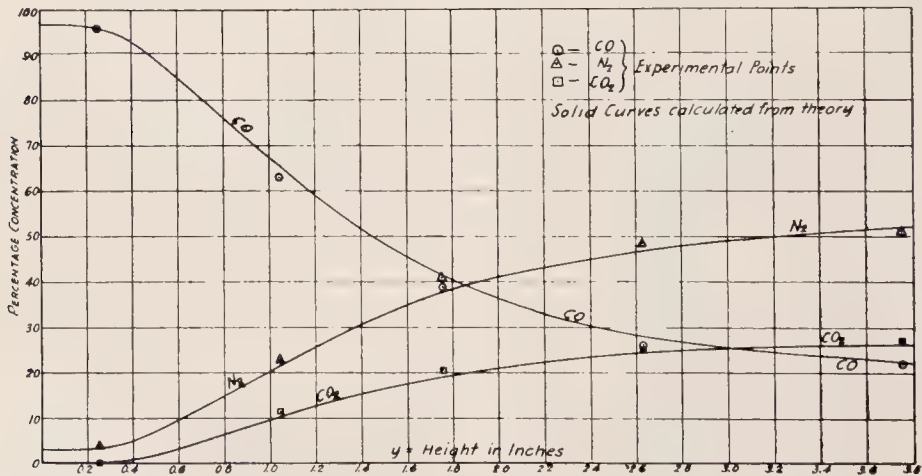


FIG. 8. Curves showing concentrations of carbon monoxide, nitrogen, and carbon dioxide on axis of a cylindrical carbon monoxide flame.

TABLE VIII

<i>R</i> , in.	<i>L</i> , in.	Air, cu ft/hr	Carbon mon- oxide, cu ft/hr	Flame height	
				Experi- mental, in.	Theo- retical, in.
0.63	0.42	4.2	3	0.92	0.94
0.63	0.42	8.0	6	1.75	1.75
0.63	0.42	3.25	3.75	1.02	1.02
0.63	0.42	5.55	6.25	1.75	1.76

analysis the value of the coefficient of diffusion of carbon monoxide was calculated to be 0.104 square inch per second according to the procedure described above. This value was used to determine the theoretical heights of a number of carbon monoxide flames. In Table VIII the data concerning these flames together with their measured and calculated heights are given.

In the last two experiments the flame was "inverted"—i.e., air was passed up the inner tube

and carbon monoxide up to the outer tube. The agreement between the experimental and calculated heights of these monoxide flames needs no further comment.

Conclusions

The theory of diffusion flames proposed herein shows such good agreement with the experimental facts that we feel justified in the hope that its adoption, in essentials at least, may lead to a better understanding of, and further contributions concerning, this very common and interesting class of flames. The authors feel that a more fundamental investigation of the phenomena described here on the basis of the kinetics of the chemical reactions involved might yield both interesting and profitable results.

Acknowledgments

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MEASUREMENT OF THE TEMPERATURES OF STATIONARY FLAMES*

A. G. LOOMIS AND G. ST. J. PERROTT

Flame Laboratory, Pittsburgh Experiment Station, U.S. Bureau of Mines, Pittsburgh, Pennsylvania

The concept of temperature as applied to flames is discussed. A number of proposed methods for measuring the temperatures of flames are critically reviewed and the optical method of Kurlbaum-Fery is described and examined in detail. This method depends upon comparing the brightness temperature of a continuous radiator with the brightness of the radiation from the flame colored with an alkali-metal vapor at a given spectral line. From a consideration of the laws of radiation it is shown that the true flame temperature is equal to the brightness temperature of the comparison radiator, as read with an optical pyrometer, when the spectral line is just reversed as seen in a spectrometer.

Curves representing flame temperature as a function of air-gas ratio as measured by the line-reversal method are given for Pittsburgh natural gas, methane, propane, and carbon monoxide. These results are compared with measurements depending on the flame gases heating a solid radiator contained in the flame and with the calculated results for the maximum temperature attainable at complete combustion.

An investigation of the temperature of stationary flames is being carried on at the Pittsburgh Experiment Station of the U. S. Bureau of Mines in connection with studies of flame propagation. Experiments are being made with stationary flames preliminary to measurements on flames produced by coal-mine explosives. Although Kurlbaum¹ in 1902 described a method for the measurement of the temperature of carbon-containing flames such as the candle, illuminating gas, and acetylene flames, nevertheless very few measurements of the temperatures of stationary flames are recorded in the literature. Recourse is taken to the calculated flame temperature, utilizing the ΔH of the reaction, the specific heats of the products, and the degrees of dissociation of carbon dioxide and water. Owing to our lack of knowledge of the true specific heats, especially above 2000°C, and particularly the amount of radiation from a given flame, these calculated maximum temperatures must bear an uncertain relation to the actual temperature. It is highly desirable, therefore, to measure the temperatures of flames under known conditions of air-fuel ratio, design of burner, etc., and to supplement these measurements of temperature with radiation measurements under exactly the same conditions. In this paper some of the established methods of flame temperature measurement are compared and the results obtained with several gases using an optical method due to Kurlbaum, as modified by Fery.

It is generally stated that a flame cannot have a temperature in the strict sense of the word, because it is not a system in equilibrium. Chemical reactions are taking place; part of the energy may be radiated by chemiluminescence and a

certain time taken for the transformation of the remaining energy into kinetic energy of the products.

Ames² says that "for a body not in a state of statistical equilibrium, it is not allowable to use the word 'temperature.' This means that the word should not be used with reference to a single molecule or to such phenomena as occur in most flames, or in an electric spark or discharge. It is true that bodies placed in flames, sparks, etc., may assume definite temperatures, but this does not affect the statement just made."

Haber³ believed, however, that the region of a flame in which reactions are taking place is confined to surfaces—for example, the boundary of the inner and outer cone of a Bunsen flame—and that in the main body of the flame little reaction is taking place and thermal equilibrium may be nearly attained. He has shown that the water-gas equilibrium adjusts itself very rapidly in the flame of a Bunsen burner, and has calculated the temperature in the inner cone from gas analyses made in the flame separator of Smithells and Ingle.⁴

Maxwell conceived the temperature of a body as "its thermal state considered with reference to its power of communicating heat to other bodies." If we made this our criterion of flame temperature, we might employ as the other body a thermocouple inserted in the flame. Values obtained by this means differ from one another depending on the size of the couple, but to a certain extent corrections may be made for this variation. Other possibilities arise in connection with measurements of radiation from flames, and it appears that for certain wavelengths, at any rate, a flame sufficiently thick may radiate as a black body. The method of spectral-line reversal finally adopted by the writers seems to be most

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free from theoretical objections, and the experimental manipulations involved are made easily and rapidly. The various methods employed by other workers are discussed in the following text.

Methods Used by Other Investigators

Several well-recognized methods may be used for such measurements. Nichols⁵ introduced thermocouples into the flame to various accurately measured distances from the median plane of the flame and by extrapolating to distance zero found $t=1750^{\circ}\text{C}$ for the middle of the Bunsen flame and also the temperature gradient in the flame. Waggener⁶ introduced platinum, platinum-rhodium thermocouples of decreasing thickness into the flame and by extrapolation to a thermocouple of zero thickness corrected for loss due to conduction and radiation, obtaining 1750°C for the Bunsen flame.

Burkenbusch⁷ likewise introduced a thermocouple directly into the flame and compensated for heat loss by radiation by heating the wire electrically. To accomplish this he represented the watt-consumption of the couple as a function of its temperature when suspended in a vacuum. The couple was then suspended in the flame and again electrical energy was added and represented as a function of the temperature of the couple, giving a curve that was of less slope than the first curve. The intersection of these two curves was taken as the temperature of the flame, because the radiation loss was assumed to be the same in each case, and when the couple and the flame are at the same temperature no heat is added from nor lost to the surrounding gases, a condition entirely duplicated *in vacuo* where there is no gas or such addition or loss of heat.

This method was approved by Schmidt.⁸ Instead of a thermocouple he used a platinum wire, measuring its temperature optically and determining its heat loss by radiation in absolute units when heated electrically outside the flame by measurements with a thermopile. Inside the flame the consumption of electrical energy was measured at the same time as the temperature of the wire (optically); this was likewise put in absolute units and the sum of the loss through radiation and convection given. His measurement by this method gave 1800°C at the hottest point of the Bunsen flame. It is not clear how Schmidt corrected for heat lost by convection when the wire was heated in air.

A method recently proposed from the National Physical Laboratory⁹ is quite similar to the method of Schmidt. A refractory metal in form of wire is heated electrically *in vacuo* and the relation between temperature and heating current is determined by an optical pyrometer. The same

wire is then inserted into the flame and the relation between temperature and heating current is again determined. When the results are plotted graphically the point of intersection of the two lines is assumed to give the temperature of the flame, for at the temperature represented by this point the electrical supply is sufficient to balance the radiation loss, whether the wire is *in vacuo* or in the flame, so that the surrounding gas in the flame neither imparts nor abstracts heat from the wire. The temperature of the Bunsen flame measured by this method was 1765°C .

A sample of the gases undergoing combustion may be withdrawn from the flame at given points through a water-cooled tube for analysis and, together with the heat of combustion, the specific heats of the combustion products, and equilibrium data, the temperature may be found, as was done by Haber and Hadsman¹⁰ in the case of the acetylene-oxygen flame.

The conductivity of the flame containing a known concentration of an alkali salt may be measured, and from this the equilibrium constant K of the reaction $\text{M} \rightarrow \text{M}^+ + e$ is calculated. The equilibrium constant for the ionization of a metal vapor is connected with the temperature by means of Saha's equation¹¹

$$\log_{10} K = (-5048/T) V + 2.5 \log_{10} T - 6.56,$$

where V is the ionization potential of the metal vapor present in the flame. Measurements of this kind with coal-gas flames have been made by Barnes¹² and by Bennett¹³ who, however, were not making measurements of flame temperatures, but rather proving the validity of Saha's equation.

The general method of measuring the emissive and absorptive power of the non-luminous flame may be used, since the radiation spectrum of such flames contains the bands of carbon dioxide and water in the infrared. Schmidt¹⁴ found that the law of black-body radiation held quantitatively for both bands at 2.7μ and 4.4μ . From the measured values of the emissive and absorptive power of the Bunsen flame in the field between $\lambda = 2.41 \mu$ and $\lambda = 4.6 \mu$, Schmidt was able to obtain the true temperature of the flame, making use of the radiation laws of Kirchhoff and of Planck. Henning and Tingwaldt¹⁵ have very recently used this method to measure the temperature of the acetylene-oxygen flame.

It will be noted that all of the above methods except those of Kurlbaum-Fery and of Schmidt are strictly limited to flames whose temperatures lie below 1800°C , because no material that does not melt or oxidize may be used for thermocouples or electrodes or wires, while a water-cooled tube introduced into the flame to remove samples of

gas for analysis may cause serious errors due to conduction and radiation. The method of Schmidt in the infrared is difficult to apply and demands very special equipment. Thermocouples of platinum, platinum-rhodium are easily contaminated by the flame and very erroneous results are obtained from this cause; and there will always be the question of catalytic action due to any material introduced into the flame with attendant abnormal temperatures.

Method of Line Reversal

The optical method of Kurlbaum¹ subsequently modified by Kurlbaum and Schulz,¹⁶ and by Fery¹⁷ may be used at any temperature above 900°C, and has recently been used by Henning and Tingwaldt¹⁸ to measure the maximum temperature of the acetylene-oxygen flame, 3100°C. The method of Kurlbaum-Fery is one in which a continuously radiating body, such as a tungsten band lamp or an electric arc, is viewed through a spectrometer, with the flame colored by means of an alkali-metal salt, between the radiator and the spectrometer. The method may be understood by reference to Fig. 1. The tungsten band lamp *a*, serving as the continuous radiating body, is heated from a set of storage batteries by means of appropriate resistances and is focused by means of lens *b* into the center of the flame *c*, just above the tips of the cones. The brightness temperature of the band lamp is read by means of the optical pyrometer *f*, the screens *g* and *h* allowing radiation to emerge from the same point of the band. The image of the band together with the flame is focused on the slit of the spectrometer *e* by means of the lens *d*. A screen, *i*, allows radiation from an area of the flame equal to the area of the band-image to reach the spectrometer. The pair of spectral lines from the flame colored with sodium chloride vapor at $\lambda=0.589\ \mu$ are seen as bright lines upon the continuous spectrum from the comparison radiator if the latter is cooler than the flame; but if it is hotter the bright lines are reversed and appear dark upon the brighter background of the continuous spectrum. Final adjustment is made by the observer at the eyepiece of the spectrometer with the rheostats controlling

the heating current through the comparison radiator until the lines are just at the point of reversal. The brightness temperature of the comparison radiator now is the same as the temperature of the flame, and this temperature is determined by means of the optical pyrometer, keeping the current constant through the band lamp.

Theory of Method of Line Reversal

At exact reversal the following relation must hold

$$E_F + P_F E_R = E_R, \quad (1)$$

where E_F and E_R are the respective spectral brightnesses of the flame and the comparison radiator for the wavelength λ , and P_F is the permeability of the flame at the same wavelength. If the absorptive power of the flame is given by A_F and the reflective power as R_F , then we have

$$E_F/A_F = (1 + R_F/A_F) E_R, \quad (2)$$

since $R_F + P_F + A_F = 1$. If the reflective power of the flame is so small that it may be neglected in comparison to the absorptive power, then

$$E_F/A_F = E_R. \quad (3)$$

From Kirchhoff's law it follows from Eq. (3) that the true flame temperature is equal to the true temperature of the comparison radiator, if this is a black body, or to the apparent temperature as measured by an optical pyrometer if the radiator is not a black body.

Three possible questions arise with the method outlined: (1) Does the temperature of the flame remain unchanged when it is colored with a metal salt? (2) Does Kirchhoff's law apply accurately to emissive and absorptive processes for a spectral line? (3) Can the reflective power of the flame be neglected when it is colored with a metallic salt?

(1) It was shown by Kohn¹⁹ that for the Bunsen flame the same temperature was obtained within the experimental error (10°) with the line-reversal method, the flame being colored with a sodium salt, and for the noncolored flame using the method of Schmidt, as outlined above. This was also proved by Henning and Tingwaldt¹⁵ in the case of acetylene-oxygen flames by measuring the total radiation from the colored and non-colored flames by means of a vacuum thermoelement.

(2) Kirchhoff's law as embodied in Eq. (3) can apply only when the emissive power E_F and the absorptive power A_F of the flame apply to exactly the same process—that is to say, it is necessary for a given spectral line that the absorbed energy be completely converted into heat or radiation of the same wavelength, and

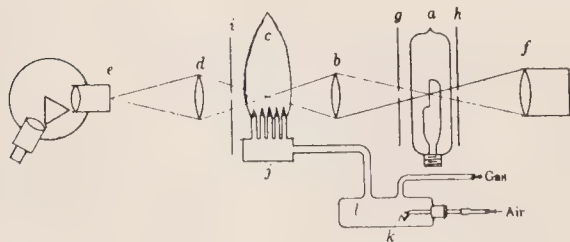


FIG. 1. Line-reversal apparatus.

conversely the energy emitted in the particular spectral line must represent only the heat of the molecule or the absorbed energy at the same wavelength. It is necessary, therefore, in measurements by the line-reversal method to deal with spectral lines for which in emission as well as in absorption reversed energy transitions are possible—that is, resonance lines, such as the sodium D-lines, the red line of lithium, or the green line of thallium. The conception of a resonance line implies (1) that its final orbit is the ground orbit of the atom, and (2) that its initial orbit is the (energetically) next highest orbit from which the return to the ground orbit, and only to this, is possible, being accompanied by the emission of monochromatic light. The heat energy from the combustion processes in the flame containing an alkali-metal vapor will lift the electron from its ground orbit, $1 S$, into the “energetically” next highest orbit, $2 P$. According to the principle of selection the atom thus excited can undergo the transition $2 P \rightarrow 1 S$ as the only way in which the excited atom can revert to its unexcited state, thus giving out monochromatic light of the same wavelength as it absorbed. It is clear from this that only resonance lines may be used, for Kirchhoff’s law would not apply in cases where intermediate quantum states are possible; and in that case the true flame temperature would not be equal to the brightness temperature of the comparison radiator.

In measuring the temperature of luminous gases it is also necessary to take into account whether the radiation intensity observed is due entirely to the kinetic energy of the molecules or in part to chemical or electrical processes of some kind, for in the case of chemiluminescence the laws of radiation cannot apply. For example, the radiation equation of Planck is derived explicitly from the assumption that the vibrating resonators obtain their energy from the heat motion of the molecules, and only in that case can kT be substituted for the average energy \bar{U} of a resonator. In cases of chemiluminescence we should have to put in place of kT a function $f(i)$ of the intensity i of the process excited by luminescence, and T would therefore disappear from the radiation equation.²⁰ Kohn¹⁹ has definitely shown by measurements of emissive and absorptive powers within the range 900° to 1800°C that Kirchhoff’s law quantitatively applies to flames colored with alkali-metal vapors, and therefore they are pure temperature radiators and chemiluminescence effects are entirely absent. In general, the condition for pure temperature radiation will be more nearly approached the higher the temperature of the flame under the same conditions otherwise,²¹ and this fact makes possible the measurement of flames with very high temperatures such as the

acetylene-oxygen flame, by the line-reversal method.

(3) It was proved by Henning and Tingwaldt¹⁸ by experimental measurement that the reflective power of such colored flames is zero. We should expect this result from the work of R. W. Wood, who has shown that a very high concentration of mercury vapor is necessary for metallic reflection, whereas in these flames we are dealing with very low concentrations of metal vapors.

It is evident that the method of line reversal has much to commend it from the theoretical standpoint. It gives values indicating the ability of the flame to impart heat to the sodium atom and, owing to the intimate mixture of the metal atoms with the reacting gases of the flame, temperature equilibrium should be established rapidly and the values determined by this method should approximate the true temperature of the flame. From the experimental standpoint the method is ideal because of the simplicity of the experimental technic and the rapidity with which the measurements may be made.

Experimental Method

The burner j (Figure 1) consisted of a small brass box containing three rows of five quartz tubes in a row, each tube 5 mm in diameter, except for the measurements with carbon monoxide when the diameter of each was 4 mm. The tubes were completely encased with asbestos paper to prevent the introduction of secondary air from below. The sodium chloride solution (just under saturation) was sprayed into the flame by means of a small glass nozzle, k , of the type used by Barnes¹² and by Bennett.¹³ The gas stream entered the mixing chamber l directly at the source of the air stream, insuring complete mixing. The gases were introduced either from cylinders containing the gas under pressure or from a large gasometer and pumped into the mixing chamber by means of a small gas-tight pump at rates that could be determined on a sensitive orifice flowmeter. The air was supplied from a large pump at rates read on a second orifice flowmeter. Both gas and air were passed through several large bottles to smooth small pressure fluctuations. Samples of the gas-air mixtures were drawn off for analysis just before entry into the burner. These analyses were made on a Bone-Wheeler apparatus.²²

The brightness temperature of the tungsten band lamp, after the adjustment to line reversal as described above, was read on an optical pyrometer of the disappearing filament type. It was calibrated against a pyrometer of the rotating-disk type which had been calibrated by the

Bureau of Standards. Readings were made through a red ($\lambda=0.665 \mu$) filter glass as usual, and since the brightness comparison in the spectrometer was made in the yellow ($\lambda=0.589 \mu$), a correction is necessary. By employing the relation between true temperature T and brightness temperature S_λ , as derived from Wien's equation, we have

$$T^{-1} - S_\lambda^{-1} = \frac{\lambda \cdot 2.303 \log e_\lambda}{c_2}$$

and

$$T^{-1} - S_{\lambda'}^{-1} = \frac{\lambda' \cdot 2.303 \log e_{\lambda'}}{c_2},$$

where λ refers to red light (0.665μ) and λ' to yellow light ($\lambda=0.589 \mu$), e_λ the spectral emissivity, and $c_2=1.433$ cm deg. Subtracting we have

$$S_{\lambda'}^{-1} = (2.303/c_2) [\lambda \log e_\lambda - \lambda' \log e_{\lambda'}] + S_\lambda^{-1},$$

where S_λ is the brightness temperature observed with the pyrometer and $S_{\lambda'}$ is the temperature of the flame. From the data of Forsythe and Worthing²³ for spectral emissivities of tungsten as a function of the true and the brightness temperature, transposition curves were plotted for the temperature range covering these experiments, and this additive temperature (from 25° to 32°C, depending on the temperature) applied as a correction to the readings.

The absorption of lens b was determined by focusing the pyrometer on the image of the band lamp and then on the band lamp directly, with the lens removed. This absorption amounted to 29°C, and is a negative correction to the flame temperature, just about canceling the color correction described above.

The cooling effect of the water in the salt-solution spray was found experimentally by inserting a platinum strip in the nonluminous flame and reading its temperature on the pyrometer, with and without pure water being sprayed at the same rate as used in the measurements with the flames. The amount of cooling was 15°C for all the flames except the carbon monoxide flame, where it was 5°C because less air was used. The measurements of Henning and Tingwaldt¹⁸ showed that the salt in the spray had no cooling effect.

Gases

The methane was obtained from a natural-gas well and analyzed 97 per cent CH_4 ; the propane was of commercial grade. Both gases were stored in cylinders under pressure. The Pittsburgh natural gas (85 per cent methane, 14 per cent

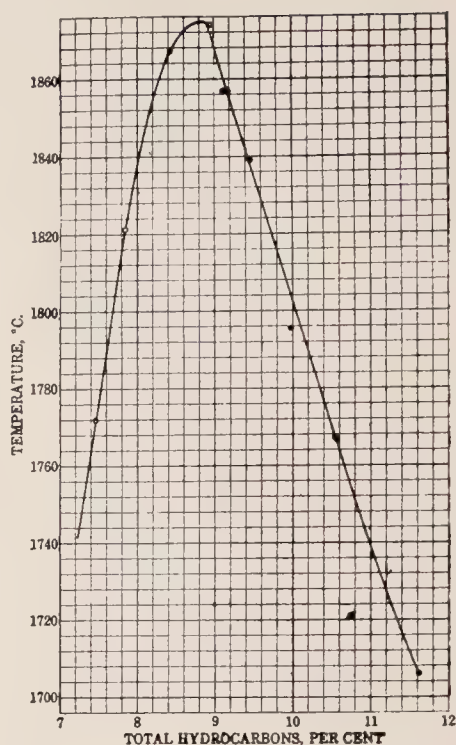


FIG. 2. Pittsburgh natural gas.

ethane, 1 per cent nitrogen) was taken from the city mains. The carbon monoxide was prepared from formic acid, dehydrated by phosphoric acid, and purified with potassium hydroxide solution together with an absorbing tube of Carboxide and charcoal; its purity was better than 99 per cent by analysis.

Results

The results of the measurements by the line-reversal method are shown in Figs. 2, 3, 4, and 5. The corrected temperature is plotted as a function of per cent gas in the gas-air mixture, except in the case of Pittsburgh natural gas where per cent total hydrocarbons is plotted.

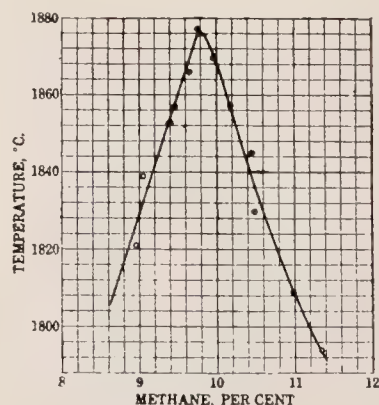


FIG. 3. Methane.

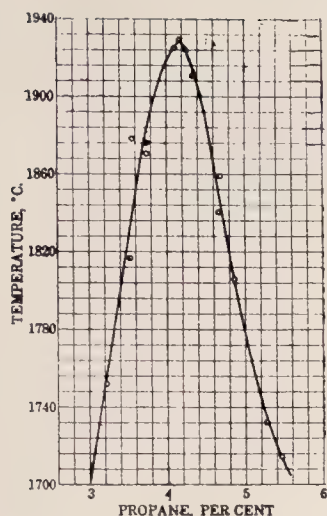


FIG. 4. Propane.

Comparison with Solid Radiator in Flame

It was thought advisable to compare the results by the line-reversal method with measurements by another method that should differ from it as much as possible. The method as proposed by the National Physical Laboratory as outlined in the introduction, was chosen, using a natural gas-air mixture of 10.83 per cent total hydrocarbons, which gives a temperature of 1750°C according to the method of line reversal. The intersection of the curves of temperature as a function of heating current when using a bright platinum strip gave 1770°C when corrected for emissivity.

The agreement to within 20°C between the two methods is regarded as satisfactory when it is remembered that they are so different in character, the one depending upon a comparison of brightness temperatures of a tungsten radiator and of sodium vapor radiating due to the temperature that it assumes from the gases of the flame, the other depending upon the heat gained by a solid radiator, corrected for radiation loss, from the flame gases. The method of line reversal is much more convenient and rapid, however, and from an experimental standpoint would be chosen in preference to all others.

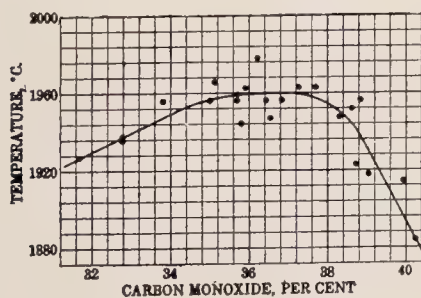


FIG. 5. Carbon monoxide.

Comparison with Calculated Temperatures

It is interesting to compare the measured values of temperature with the calculated temperatures. The calculations were based upon the ΔH of the reaction and the specific heats of the gases, both from the data of Lewis and Randall, and taking into account the degrees of dissociation of water and carbon dioxide. Calculated maximum temperatures are as follows: Pittsburgh natural gas, 2000°C; methane, 2000°C; propane, 2050°C; and carbon monoxide, 2230°C; the measured values, 1875°C, 1875°C, 1930°C, and 1960°C, respectively. The difference is due to the radiation from the particular flame under investigation, and to possible inaccuracy of the specific heat data.

It is to be noted that the maximum temperatures as measured correspond to gas-air mixtures somewhat higher than the theoretical mixtures for complete combustion. This is perhaps due to the fact that some air is drawn into the flame from the surrounding atmosphere.

Further measurements are under way for many other combustible gases, mixed with air and with oxygen. It is planned to measure the temperature of these flames with various designs of burners, and supplement these measurements of temperatures with measurements of total radiation.

Acknowledgments

The writers' thanks are due to J. E. Crawshaw, explosives engineer, for his assistance in making temperature calculations, and to J. S. Brown, junior explosive chemist, who assisted in the experimental measurements.

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RADIANT ENERGY FROM FLAMES

W. E. GARNER

Department of Physical Chemistry, Bristol University, England

The thermal and the chemiluminescence theories of the radiant energy from flame are discussed and the conclusion is reached that the emission is very largely chemiluminescence. New experimental evidence on the radiation from the carbon monoxide flame is in agreement with this conclusion.

The study of the radiant energy from flames offers a line of approach to the problems of catalysis of the processes of combustion, and this is illustrated by reference to experimental work on the catalysis of the carbon monoxide flame by hydrogen. It is concluded that the action of hydrogen is twofold in character. It acts as a catalyst in the chemical sense when the hydrogen percentage exceeds 0.02, and as a conserver of chemical energy within the flame throughout the whole range of concentrations up to 2 per cent. The latter type of catalysis is termed "energo-thermic," and in the above example it is concluded that either the proton or the electron is the effective agent. The chemical energy is conserved within the flame by collisions between protons or electrons and the newly formed products of the combustion process.

The study of the radiation from flames is in the embryonic stage of development. It shows promise, however, of becoming a highly specialized branch of knowledge, which will play an important part in the elucidation of the mechanism of the processes of combustion occurring in flame.

The advance of modern physics has made us aware of the almost infinite variety of "unit mechanisms" which can occur during the interaction between molecules and between molecules and radiation. These mechanisms have been classified and certain laws concerning them have been made known. There exists, therefore, a much broader, and at the same time a more detailed, basis for the investigation of the phenomena of flame than was possible before the advent of the new ideas on the relationship between matter and radiation. A development of experimental technic for the measurement and analysis of radiant energy has accompanied the growth of theoretical knowledge, and has placed in the hands of the experimenter a variety of new weapons of attack. The application of this technic to the study of the flame offers a line of approach to its problems which will enable us to understand more clearly the mechanism of the processes of combustion which intrigued the minds of van Helmont and Hooke several centuries ago.

Chemiluminescence from Flame

The source of the radiant energy from flames is the chemical energy set free during the oxidation of combustible substances. This energy is transformed by a chain of molecular processes into the energy of chaotic motion; at some stage in the chain of reactions and collisions radiant energy is emitted. R. von Helmholtz,¹ Paschen,² Pringsheim³ and others have tried to determine at what

stage in this series of processes the emission of energy occurs, but have been unable to come to an unequivocal decision, even with regard to the main points at issue. Helmholtz and Pringsheim have favored the view that the radiant energy is emitted during or directly after the chemical change—i.e., that it is chemiluminescence—but Paschen has regarded it as a purely thermal phenomenon which was solely a consequence of the high temperature of the gaseous products. On the second view the emission of radiation does not occur until the energy of chemical combination has been completely converted into thermal energy. The experimental evidence was not decisively in favor of either hypothesis, but as a result of the controversy that ensued a number of important facts have been established concerning the nature of the oscillators emitting the radiation from flame.

A comprehensive study of flame spectra, undertaken by Julius¹ in 1889, brought out the main difference between the radiation from flames and that from hot solid bodies; the spectrum of a flame consists of sharply separated bands lying mainly in the infrared portion of the spectrum. Julius made the important discovery that the position of these bands depended on the products of the combustion and not on the nature of the combustible. For example, in the radiation from the hydrocarbon flame was a band at $4.4\ \mu$ which was characteristic of the flame of carbon monoxide, and another band at $2.8\ \mu$ was common to hydrocarbon, carbon monoxide, and hydrogen flames. The hydrocarbon flame spectrum is in fact composite in character, consisting of two superposed spectra, the one identical with the spectrum of the carbon monoxide and the other with that of the hydrogen flame.

R. von Helmholtz came to the conclusion that the emitters of the radiation in hydrocarbon

flames were the gaseous products—i.e., carbon dioxide and water. He further suggested that the amount of radiation from such flames was proportional to the mass of carbon dioxide and water formed. In the second conclusion, however, he was at fault, and he has been adversely criticized by Haslam, Lovell, and Hunneman⁴ on the ground that the amount of radiation depends on the amount of aeration of the flame.

Paschen made the discovery that water vapor and carbon dioxide, when heated to a high temperature, gave out radiation with band maxima at the same wavelengths as the maxima for the hydrocarbons, carbon monoxide, and hydrogen flames. This he held to be conclusive proof of the thermal origin of the radiation. Paschen also drew attention to the fact that the band maxima occurred at very nearly the same positions as the absorption maxima previously observed by Ångström⁵ for carbon dioxide.

These observations admit of only one interpretation; they prove that the oscillators emitting the radiation from hydrocarbon flames are molecules of carbon dioxide and water. They leave undecided, however, whether or not the emitters are in a state of thermal equilibrium, as was maintained by Paschen. All that has been demonstrated is that thermally excited molecules give the same spectrum as that of the same molecules when excited in the flame. It is still possible, however, to maintain the theory that the products of reaction lose a portion of the internal energy which they acquire as a result of chemical change, directly as radiation, and it is equally allowable to hold Paschen's view that thermal equilibrium is so rapidly attained in the flame that the bulk of the radiation is emitted by carbon dioxide molecules activated by collision.

R. von Helmholtz devised an experiment which he considered would give an unequivocal decision on the merits of the two hypotheses. He attempted to raise the flame temperature by preheating the gases, and found that the radiation was not augmented as would be expected according to the thermal theory, but that there was a decrease in intensity, which is an effect predictable from the theory of chemiluminescence. Haslam, Lovell, and Hunneman⁴ have repeated the experiment with a similar result, but they point out that it is inconclusive on account of the preliminary reaction, which may occur during the preheating, which would lower the chemical energy available in the flame itself, and thus lower its temperature.

It is possible to lower the temperature of the flame by admixture of inert gases with the combustible substances, and on the thermal theory this should lower the intensity of emission of radiation. Complications will arise, however,

if the diluents themselves emit or absorb radiation. Nitrogen, hydrogen, and oxygen at room temperature do not absorb radiation in the infrared region of the spectrum, and hence these substances might be suitable diluents for tests of the existence of chemiluminescence in the radiation from flames. F. Roffey, at Bristol University, had made measurements of the effects of the addition of nitrogen, oxygen, and hydrogen on the intensities of emission from carbon monoxide and oxygen; the mixtures were ignited in a closed tube 80 cm in length, and the radiation emerging through a fluorite window allowed to fall on a thermopile.⁶ The pressures were so adjusted that equal amounts of combustible were burned in each experiment. The results for nitrogen and oxygen are given in Table I. In both cases the emissivity is increased in spite of the large decrease in temperature which occurs on the addition of the diluents. These experiments support the theory of chemiluminescence, but afford no certain proof, for nothing is known of the emissive power of oxygen (Paschen showed that at 1500°C the emissivity of air is negligible) and nitrogen or oxides of nitrogen at the temperatures of the flame.

Hydrogen exerts a very marked effect on the emission from a carbon monoxide flame; the radiation is diminished sevenfold by the addition of 2 per cent hydrogen to a carefully dried mixture and even 0.005 per cent of hydrogen produces a marked fall in the emission from the flame (Curve I). Hydrogen accelerates the speed of movement of flame, as was shown by Dixon⁷ and if present in small amount it increases the explosion pressures obtained in closed vessels. The temperatures of the flame would therefore appear to be somewhat higher after the addition of hydrogen than before. Since the effect cannot be due to a change in temperature, the action of hydrogen can only

TABLE I
Total radiation from flame

Composition ^a	Pressure, atm.	Total radiation ^b
2CO + O ₂	1.00	21.7
2CO + 2O ₂	1.33	23.6
2CO + O ₂ + N ₂	1.33	25.1
2CO + O ₂	0.75	19.2
2CO + 3O ₂	1.25	20.1
2CO + O ₂ + 2N ₂	1.25	21.5

^a All the mixtures contained 0.01 per cent H₂.

^b Radiation is given in arbitrary unit.

be explained on Paschen's view, by the assumption that the thermal emissivity of carbon dioxide is lowered by the presence of hydrogen.

Let us consider the nature of the action of hydrogen on carbon dioxide which is required in order that the above results may be explained on the thermal hypothesis. The two gases, carbon dioxide and hydrogen, will be imagined to be contained within an enclosure which is a perfect black body. The temperature will be that of the flame, and the hydrogen will be very largely present as atoms and a small fraction as protons. Let it be assumed that collision with hydrogen atoms decreases the thermal emissivity of carbon dioxide. Certain equilibrium conditions must be maintained within the enclosure. According to the "principle of microscopic reversibility," every unit mechanism must be reversible. Thus, a molecule of carbon dioxide which is capable of emitting radiation of a given frequency must also absorb radiation of the same frequency. At equilibrium the rate of the process of emission must equal the rate of the process of absorption of radiation. It follows, therefore, that if the emissivity of molecules of carbon dioxide is reduced by the presence of hydrogen, the rate of absorption must be reduced to the same extent. A collision between hydrogen and carbon dioxide molecules must be such that during the very short duration of collision an effect is produced which persists over the interval between successive collisions. This effect is such that it renders a molecule of carbon dioxide less capable either of absorbing or emitting radiation. If the hydrogen concentration is 0.005 per cent, the effect of a collision of a hydrogen atom with a molecule of

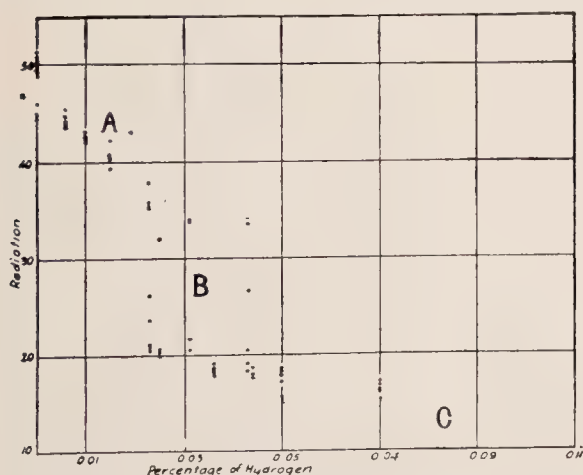
carbon dioxide must persist throughout, on an average, 10,000 collisions with carbon dioxide molecules. Such an effect is inconceivable. (When the absorbing substance is in small concentration in the presence of large concentrations of inert gases, the extinction coefficient may be affected as was shown by Meeke for carbon dioxide.) It does not appear to be possible to explain the radiant energy of flames and the effects of hydrogen on the emissivity of the carbon monoxide flame in terms of Paschen's theory.

Catalysis of Movement of Flame

An acceleration or retardation of any one of the unit mechanisms in the chain of reactions and collisions which occur during the conversion of chemical energy into thermal energy may modify the speed of movement of flame. Some of these unit mechanisms may involve a chemical change, and others merely a transference of energy from one molecule to another. These two distinct types of unit mechanisms occurring in the flame, the one chemical and the other physical in character, will each give rise to its own type of catalytic effect.

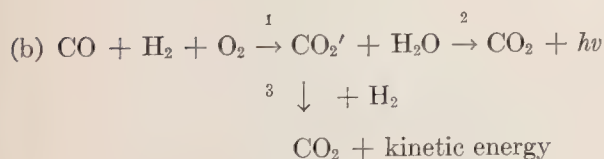
The reaction chains commence in the cold gases entering the flame and cease only when the gaseous products have cooled far below the maximum temperature of the flame. The speed of movement of flame may be influenced by changes in the preflame zone as well as in the flame itself. The catalysis occurring in the pre-flame period has been very successfully investigated by Callendar and Mardles⁸ and by Egerton,⁹ who have shown how the elaboration of the reaction chains in petrol-air mixtures may be interrupted or accelerated by the presence of catalysts. The reactions in the pre-flame period are often sufficiently slow to be investigated by streaming methods. In the flame itself, the reactions occur very rapidly and we have little save physical methods available for their investigation. The examination of the spectra of the flame in the ultraviolet, visible, and infrared regions and measurements of ionization are almost the only means we have of studying the chemical processes occurring in flames.

As an illustration of the utilization of measurements of infrared radiation for the study of catalysis in flame, it is proposed to give an account of some measurements on the carbon monoxide flame made by Johnson^{6,10} and Roffey.¹¹ The movement of this flame is accelerated by any hydrogen-containing substances, and is retarded by substances that remove traces of these vapors. Acceleration of the speed of movement of flame is found to be always accompanied by a decrease in the intensity of emission of radiation and a



Curve I. Effect of hydrogen on the radiation from carbon monoxide-oxygen explosions. The galvanometer deflections are plotted against the percentage H_2 . In the upper part of region A the radiation is not exactly proportional to the galvanometer deflections.

At this stage we can only speculate as to the nature of the two mechanisms. The general character is probably that shown below:



The action of hydrogen is very exceptional; no other substance reduces the radiation from the flame, and this indicates the presence of some very unusual deactivator. It might be the electron, for the ionization in the flame is increased on the addition of hydrogen. It is difficult to decide whether the deactivator is the proton or the electron. If it is the latter, then the addition of small quantities of an easily ionizable gas should speed up the movement of flame. The proton is practically a point molecule and on this account collisions between it and other molecules will present unusual features. One of these features may be the more ready conversion of molecular vibrational energy into kinetic energy.

The author is very much indebted to C. H. Johnson for collaboration in the earlier experimental work on the carbon monoxide flame, and to F. Roffey for the experimental work referred to in this paper and for calculations of the composition of the gases at the temperature of the flame.

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BUNSEN FLAMES OF UNUSUAL STRUCTURE*

FRANCIS A. SMITH AND SAMUEL F. PICKERING

204 Chemistry Division, Bureau of Standards, Washington, D. C.

An abstract of a description, illustrated by lantern slides and autochromes, of unusual flame structures, the causes for which have not yet been investigated.

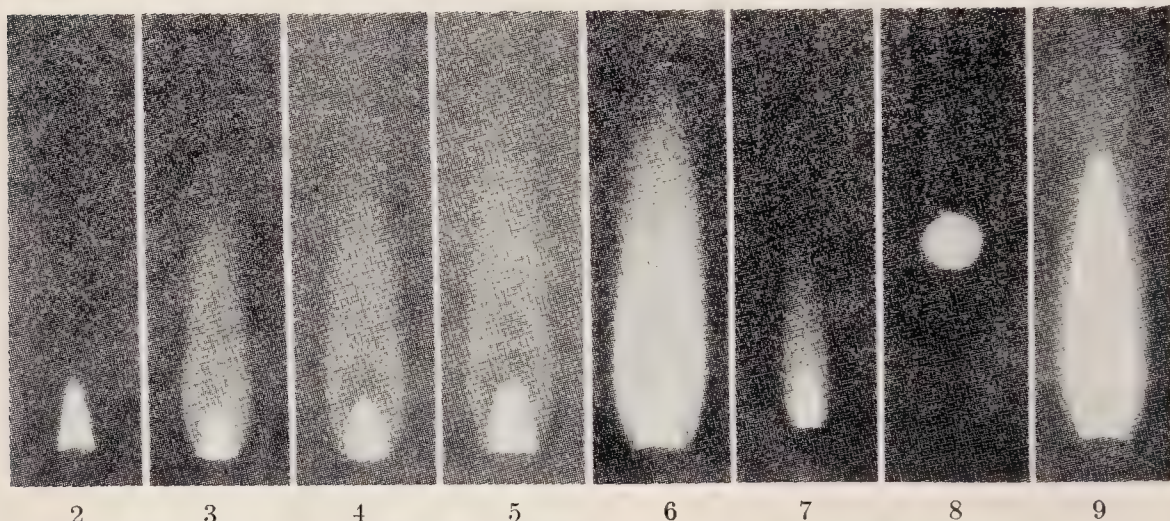
A mixture of air or oxygen with a combustible gas is forced through a burner tube, and the flame is observed as it burns in secondary air. Some examples of complex structure observed

Accurate and reproducible control of the composition and rate of flow of the gas mixtures, and very steady stream line flow in the burner tubes have been attained. Photographs of the above flames are presented herewith.

Using propane and air, when secondary air is excluded the primary zone or combustion surface presents the appearance shown in Fig. 1 (5.31 per cent C_3H_8). It is perfectly stable and reproducible. The figure can be made to rotate rapidly, slowly, or to remain stationary, depending upon the composition of the gas mixture, to which it is very sensitive.



FIG. 1. Propane-air.

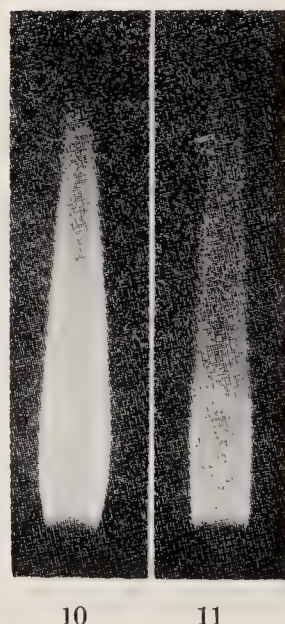


in acetylene-air flames are: four distinct zones of combustion, the intersection of two zones, and a hollow dark core extending upward from the tip of the primary zone.

When secondary air is excluded, the primary combustion surface of some hydrocarbon-air flames becomes polyhedral. Flames having three, four, five, six, and seven sides have been observed, which will rotate or remain stationary. The number of sides is a function of the size of the burner tube and of the composition of the gas mixture.

Burning in secondary air, the primary zone of some propane-oxygen flames becomes polyhedral, and luminous streamers rise from the tip and corners of the figure, which can be made to rotate slowly, rapidly, or remain stationary.

* Publication approved by the Director of the Bureau of Standards of the U.S. Department of Commerce.



Figs. 2 to 11. Acetylene-air.

Figure 2 (5.08 per cent C_2H_2 in air) shows the primary cone with very little mantle. The mixture is almost as lean as it can be without blowing off and going out.

Figure 3 (11.67 per cent) shows much more mantle, from which the radiation is nearly uniform throughout.

Figure 4 (13.23 per cent) shows the hollow mantle, most of the light coming from its surface.

Figure 5 (15.58 per cent) shows a second inner nonluminous zone. This zone has no well-defined boundary except near the base. It is larger at the base than the primary cone, the base of which is larger than the burner tip and begins well above it.

Figure 6 (16.32 per cent) shows the beginning of a third inner zone. That portion of it which is inside the second zone is luminous.

In Fig. 7 (16.60 per cent) the third zone is distinct. Starting at the base of the primary cone, it occupies most of the second zone, intersects it, and extends outside it. The primary cone and the second and third inner zones are each surrounded by a sheath from which no light is coming. These join at their tips in a continuous dark streak which extends from the tip of the primary cone upward through the center of the flame.

Viewed from above, as shown in Fig. 8, the streak is obviously a hollow, dark center and the

sheaths appear as circles of darkness surrounding and separating the zones of light.

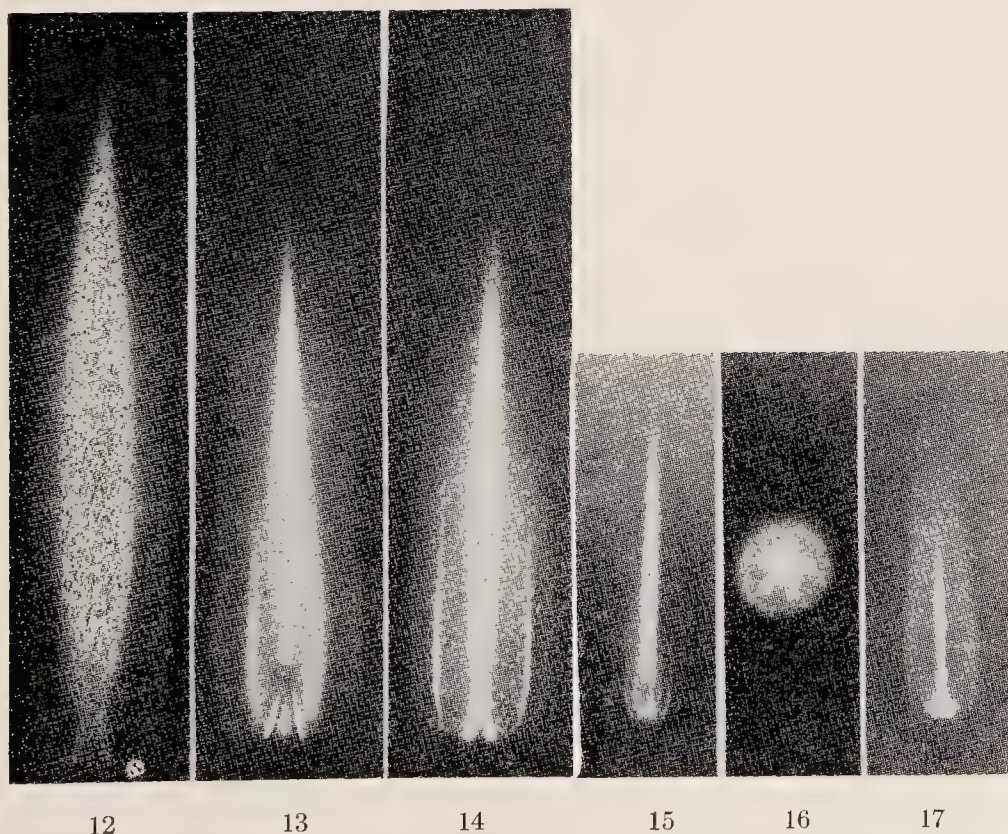
In Fig. 9 (17.73 per cent) the luminosity of zones 2 and 3 has increased, and the line of separation has disappeared except at the base, where that portion of zone 2 not occupied by zone 3 is still nonluminous. The dark core and the sheath surrounding zone 3 are still present.

Zones 2 and 3 in Fig. 10 (24.00 per cent) have increased in size and brilliance until they occupy nearly the entire volume of the flame and have almost obscured the primary cone, but a scarcely perceptible blue mantle still envelops them completely.

Figure 11 (44.75 per cent) shows the luminosity of all parts of the flame greatly reduced for lack of primary air. That which was the primary cone is now merely a region of brighter luminosity. The blue mantle which can be plainly seen at the sides is no longer continuous, and unburned carbon is escaping freely at the top.

Figure 12 is a luminous flame of propane and oxygen (33.75 per cent) with a fairly well defined primary cone surrounded by nearly uniform luminosity and with a brilliant stream rising from the tip. The entire flame is surrounded by a blue mantle.

In Figure 13 (33.40 per cent) the cone has become a four-sided figure, and the luminous



FIGS. 12 to 17. Propane-oxygen.

zone has separated into four streams which rise from the dark ridges of the nonluminous primary zone. This view, facing one side, shows the dark ridges from which no light is coming, the figure consisting merely of four disconnected sides.

Figure 14 is a diagonal view of Fig. 13, in which luminous zones resembling zones 2 and 3 of the acetylene flame are visible.

Figure 15 (32.95 per cent) shows the four-sided figure changed into one having five sides. The

luminous streams are smaller and rise from the corners of the base instead of all along the ridges.

Figure 16 is a view of Fig. 15 from above.

A little more oxygen causes the flame in Fig. 16 to begin rotating slowly, and still more causes very rapid rotation, shown in Fig. 17 (32.25 per cent), with the luminous streams, which are now much smaller, forming an apparently continuous ring at the base and extending upward like the sides of a cup.

THE FLICKER OF LUMINOUS FLAMES

D. S. CHAMBERLIN AND A. ROSE*

Lehigh University, Bethlehem, Pennsylvania

The vibratory motion of luminous flames has been studied by the photographic method. The rate of vibration, speed of flame, movement, and amplitude of vibration have been determined for various gases under different conditions. The data show that the upper portion of the luminous zone rises to a maximum height ten times per second. This rate of vibration is not greatly affected by change in conditions. The lower portion of the flame has a continuous existence, but periodically gives off another flame, which rises above the main flame during its short period of existence.

Observation of a luminous Bunsen flame shows that the flame is not in a steady state at any time, but that there is considerable motion, especially in the upper part. This is apparently true of all flames burning without primary air, from any tip or opening. Although a large amount of work has been done on the phenomena of flames in general, there has been almost no study of this vibratory nature of most flames.¹

It has been noted in flame-speed studies that the flame does not travel with uniform motion but with periodic increases and decreases of speed.² In some cases the flame travels alternately forward and backward, the backward movement being the slower. However, all such observations have been made in tubes having one end closed and which were completely filled with a mixture of combustible gas and oxygen or air at the start of the experiment. These conditions are quite different from those of a free flame burning from an orifice of any kind, and it is questionable whether the two sets of phenomena are related.

Since no explanation of this behavior of free flames was evident, a closer study was made. The photographic method was used, by means of which pictures were taken at the rate of 32 per second and developed and studied by projecting the image of the film. The results showed that the flicker consisted of a regular up-and-down movement of the middle and upper portions of the flame while the lower portion remained quite steady, and that the downward movement is extremely rapid if the flame exists at all during this stage. The upward movement is approximately that of the flame speed of the gas mixture probably present in the flame, and the rate of vibration for the flames of all the gases investigated is of the order of 10 per second. This rate is not greatly affected by the atmosphere in which the flame burns or by the tip from which the gas issues, or by the rate of flow of the gas. Furthermore, there is only one way in which the flicker can be stopped and that is by inserting a plate or similar object into the flame at or below a definite point in the flame structure. This destroys the

upper part of the flame structure and, therefore, eliminates the flicker.

Materials

The gases whose flames were studied were natural gas, hydrogen, carbon monoxide, ethylene, methyl chloride, butane, ethane, and hydrogen sulfide. All except carbon monoxide were obtained in cylinders under pressure and were practically pure. The carbon monoxide was prepared by dropping formic acid into hot sulfuric acid. The natural gas had the following composition: methane 71.2, ethane 23.3, nitrogen 4.7, carbon dioxide 0.8 per cent.

Apparatus and Procedure

The apparatus used to obtain flames suitable for photographic purposes consisted of a gasometer for supplying gas at constant pressure, a wet meter, active-carbon absorbing towers, a flowmeter, and a pressure gage. The gas was burned in a cubical asbestos box which was provided with a large quartz window. The burner was without air ports and was fitted at the top with a lava tip. Air vents at the top and bottom of the asbestos box were covered with wire gauze to prevent irregular drafts. The top opening could be adjusted to obtain the effect of a damper and thus regulate the draft through the box. An anemometer was used to measure the air entering the box. Before a flame was photographed, precautions were always taken to allow conditions in the house to become uniform.

The flames were photographed at a distance of 2.29 meters (7.5 feet) with a moving-picture camera. The focal length of the lens was 2.54 cm (1 inch), the length of a single exposure was 0.0182 second, and the shutter remained closed 0.0130 second between exposures. The interval was therefore 0.0312 second, $1/0.0312 = 32$ exposures per second. A governor on the camera prevented the shutter from opening unless the correct speed was being obtained.

The pictures were taken in series of 60 to 120 by allowing the camera to run several seconds.

* Columbian Carbon Fellow.

After a series had been photographed, the conditions were changed and another series obtained in a similar manner. In order to distinguish one series from the next, an electric light lying in front of the asbestos box was flashed on just at the end of each series.

With methyl chloride the flame refused to burn steadily of its own accord. This was remedied by constructing a special burner, the barrel of which was wound with nickel-chromium wire, so that it acted as a preheater for the gas.

The flames of hydrogen, carbon monoxide, and hydrogen sulfide are so nearly colorless that they failed to affect the film under the conditions of short exposure that were necessary. Several attempts were made to illuminate these flames (1) by adding ammonium chloride to the gas and (2) by putting sodium chloride into the flame. However, no successful films were obtained from these gases.

Qualitative Interpretation of Pictures

When the film had been developed, it was placed in the projector and the pictures were shown one at a time on a screen of coordinate paper. In this way a series of flame images such as those in Fig. 1 was obtained. It can be seen at once that successive pictures are quite different in appearance, indicating a distinct change in the flame during the closed interval of the shutter of 0.0130 second.

First of all, it will be noted that there is a distinct up-and-down motion to the flame. This can be shown also by a series of pictures in slow motion. In general, every third picture appears about the same. It is also evident that the movement is confined to the upper part of the flame. The lower third of the flame remains almost stationary while the extreme upper portion moves up and down, and the middle portion moves in and out.

Furthermore, the upward movement of the flame is much slower than the downward move-

ment. The upward movement usually requires two pictures, the downward movement never more than one. Further study shows that the downward movement must be practically instantaneous. With the camera used, each picture shows the position of the flame near the end of the period of exposure in upward movement, and at the beginning of the period in the backward or downward movement. If the flame receded gradually, there would be images of intermediate size between the tallest and the shortest. This is not the case, as a small picture always immediately follows a tall one. In certain cases a double picture (No. 3, Fig. 1) is obtained and this bears closer study. (In some cases two complete separated flames can be noticed on the same picture.) Here the shutter opened just before the flame reached its highest point, so that a faint exposure of the highest flame was obtained. Then, with the shutter still open, the tall flame entirely disappeared and another flame appeared at a much lower point (A') and again began to rise. The faint character of the tall flame and the distinct image of the small flame clearly show a short exposure and a long exposure, respectively, and completely eliminate the possibility of any gradual downward movement of the tall flames.

Quantitative Investigation of Pictures

In order to measure quantitatively the rate of flicker, the speed of the rising flame, and the total rise and fall in the flame (amplitude of vibration), the flame images were projected upon a piece of coordinate paper. The height of the highest point of the tip (A), Fig. 1, was then read off from each picture and recorded in the proper order. Observations showed that the bottoms of the flame images (D) were always projected in the same place for a given series. Since the only matter of interest was the variation in the higher point, an arbitrary base line was chosen and all the flame heights were calculated from this. The flame heights were then plotted against

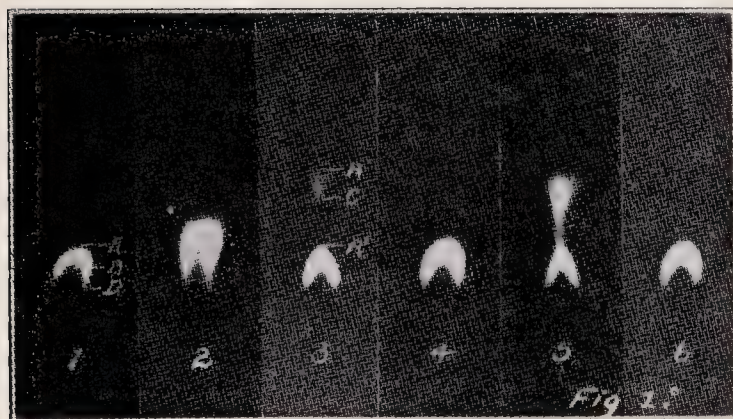


FIG. 1. The flicker of luminous flames.

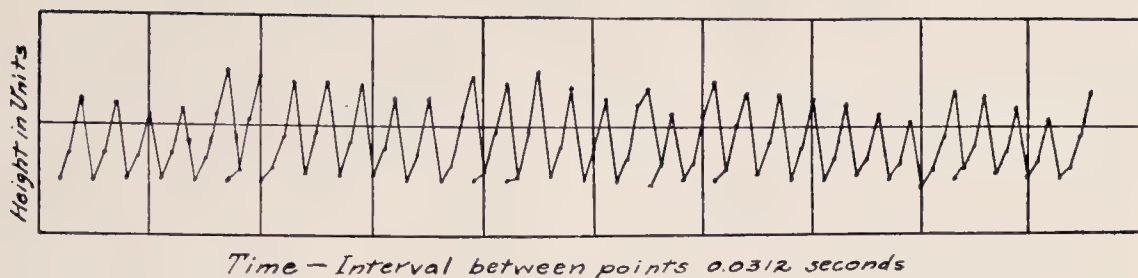


FIGURE 2.

the number of the pictures in the series, and through the resulting points a curve can be drawn as shown in Fig. 2. From double pictures of such curves it is possible to determine the rate of flicker, flame speed, and amplitude of flicker.

Calculation of Rate of Flicker

In order to calculate the rate of flicker, it is necessary to know the time elapsed during a definite number of vibrations. The time factor is easily obtained from the number of pictures being considered and the fact that the time for a single picture is 0.0132 second. The number of vibrations corresponding to a given number of pictures is more difficult to obtain accurately, because the given number of pictures rarely, if ever, corresponds to a whole number of vibrations, and there is no way of determining just what fractional part of a vibration has been neglected. Of course, if a large number of pictures are considered, the error is relatively small, but the time consumed in obtaining the data from the film is too great to make such a method practicable. The error can be reduced to negligible size if care is taken in choosing the first and last pictures of the series used for calculation. The first and last pictures must be ones in which the time of closing the shutter (end of exposure period) coincided as closely as possible with the instant when the flame reached its maximum height. The points of the curve in Fig. 2 show that successive maxima gradually decrease until a double picture is reached, and in this case the maximum height is much greater, and then the following maxima decreases gradually again. Any double picture is very nearly the picture desired for the beginning or end of a series, since here we know that the shutter closed shortly after (less than 0.0182 second) the flame reached its highest point. Then, in the following maximum the shutter must have opened just before the flame reached its maximum height. In the calculations of rate of flicker, the first and last pictures were always of the above type, so that the error involved in the calculation was a minimum.

Calculation of Flame Speed and Amplitude

The speed of the upward movement was calculated from the difference in position of the flame between two pictures and the time interval between the two pictures. The actual distance traveled by the flame was calculated from the differences shown on the curves by use of the constants of the camera and the projector and the distances used in filming and projecting. The amplitude was calculated in the same manner from the lowest and highest points of the curve for a given series.

Data and Discussion

The curves themselves are not given in the data, but only the results of the calculations. (Tables I and II) The data for hydrogen, carbon monoxide, and hydrogen sulfide have been omitted. Visible observation of these flames shows that hydrogen and hydrogen sulfide flicker, while carbon monoxide probably does although not in a pronounced manner.

Most of the data need no explanation, but before discussing and correlating the various facts it is well to point out certain significant features. In accordance with the previous work of Chamberlin and Thrun,³ the wide-slotted tip gave different results from the narrow slotted tip. The latter gave a curve very much like that obtained¹ with similar tips in a previous study. From a study of the flame-speed data, it appears that the speed of the rising flame increases as it rises.

Figure 3 represents graphically the correlation of the data obtained, in which time is plotted against height of flame. The solid line *AA* represents the upper flame boundary, the dotted line *BB* and the line *CC* the lower flame boundary. The curvature of the line *AA* represents the increase in speed of the upper flame boundary as it rises. The base line *TT* represents the height of tip. The area between the lines *TT* and *DD* represents the non-luminous lower portion of the flame, which consists of unburned gases issuing from the tip. The next higher region between *DD*

TABLE I
Data on flame flicker

Series	Pictures	Maxima	Rate of flicker, vibrations per min	Gas rate, liters/hour	Flame speed		Amplitude, cm
					Lower, cm/sec	Upper, cm/sec	
Natural gas							
Tip width, 0.089 cm							
B_1	39	13	640	16.43	32.9	56.2	3.24
B_2	a	19	607				
	b	41	609	23.51	53.1	68.5	5.73
	c	60	608				
B_3	a	26	591				
	b	42	594	67.90	49.5	63.1	5.48
	c	58	596				
B_4	a	38	607				
	b	51	603	87.82	45.7	39.6	4.48
B_5	a	24	560				
	b	41	562	79.32	36.0	41.1	3.74
	c	58	563				
B_7	a	34	564				
	b	54	568	107.65	39.0	40.3	4.23
	c	71	568				
B_8	a	37	571				
	b	54	568	99.16	35.2	42.8	3.99
	c	74	571				
Tip width, 0.025 cm							
B_9	a	14	686				
	b	46	668	10.48	12.4	14.0	1.74
	c	69	668				
B_{10}	a	41	656	19.26	35.0	41.7	3.99
	b	67	660				
B_{11}	a	38	707				
	b	57	707	39.66	27.1	37.1	2.74
	c	68	706				
B_{12}	a	29	795	73.66	Irregular		1.74
	b	44	785				
B_{13}	a	24	812	62.32	Irregular		1.74
	b	45	800				
B_{14}	a	27	783	50.99	33.7	27.9	1.99
	b	44	785				
	c	61	788				
Ethylene							
Tip width, 0.089 cm							
A_{13}	a	49	588				
	b	62	589	22.66	34.5	41.0	3.74
A_{14}	a	36	587	39.66	46.6	47.8	5.98
	b	52	591				
A_{15}	a	45	598	56.66	35.1	38.5	3.49
	b	71	595				
A_{16}	a	35	603	73.66	25.1	26.5	2.49

TABLE I—Continued

Series	Pictures	Maxima	Rate of flicker, vibrations per min	Gas rate, liters/hour	Flame speed		Amplitude, cm	
					Lower, cm/sec	Upper, cm/sec		
Ethane								
B_{17}			640	7.08				
B_{18}			592	17.00				
B_{19}			602	26.91				
Butane								
B_{20}			562	14.17				
B_{21}	a	41	12	563	25.50	44.5	57.7	5.23
	b	65	19	562				
B_{22}	a	39	11	542	39.66	40.2	58.1	5.98
	b	59	17	553				
	c	69	20	557				
B_{23}	a	25	7	537	53.83	24.5	39.3	3.24
	b	35	10	549				
	c	47	14	572				

and *BB* represents a hotter zone, where combustion is taking place and where the existence of carbon monoxide is indicated by the blue color of the flame. The next region (between *BB* and *AA*, *CC*) is the luminous portion of the flame. If a picture is taken of such a flame over a period of

time, T'_1T_1 , the result is of the type No. 1, Fig. 1, where the letters indicate the position of the several boundaries. At a slightly later time (T'_2T_2) another picture will appear as at 2. Here the luminous portion has increased in area owing to the rise of the boundary line *A*. At a

TABLE II
Effect of draft on rate of flicker of natural gas flame
(Constant gas rate, 77.91 liters per hour)

Series	Pictures	Maxima	Rate of flicker, vibrations per min	Draft, liters/hour	Flame speed		Amplitude, cm	
					Lower, cm/sec	Upper, cm/sec		
B_{25}	<i>a</i>	33	10	582	1275.0	47.8	64.7	4.98
	<i>b</i>	56	17	583				
	<i>c</i>	66	20	582				
B_{26}	<i>a</i>	29	9	596	1062.0	45.1	68.0	4.98
	<i>b</i>	55	17	593				
	<i>c</i>	65	20	591				
B_{27}	<i>a</i>	42	13	594	850.0	49.7	60.3	4.74
	<i>b</i>	68	21	593				
B_{28}	<i>a</i>	39	12	591	637.0	47.4	64.7	5.73
	<i>b</i>	52	16	591				
B_{29}	<i>a</i>	47	14	573	425.0	45.5	58.7	4.98
	<i>b</i>	67	20	573				
B_{30}	<i>a</i>	47	14	573	212.0	38.0	51.3	4.23
	<i>b</i>	67	20	573				

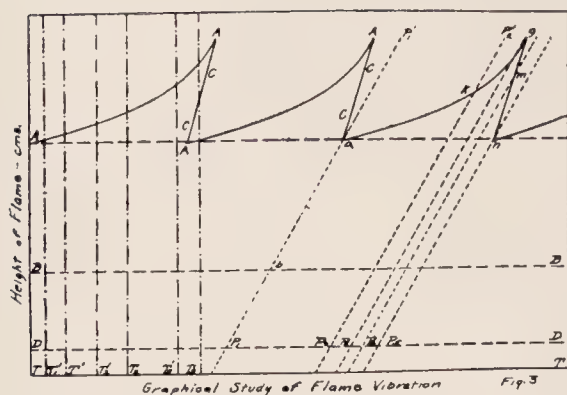


FIGURE 3.

still later time (T'_3T_3) a different type of picture (double picture) is obtained as shown in No. 3. The next picture will be of about the same kind as No. 1 and the series then repeats itself. These are just the type obtained with the moving-picture camera.

The process of combustion can be analyzed by following the gas molecules from the tip through the flame. On the diagram such molecules and their products of combustion will follow the general path of the line $P_1P'_1$. At about where $P_1P'_1$ crosses line D sufficient oxygen has diffused into the issuing gas, so that it is within its maximum limit of inflammability and combustion starts. The combustion continues with the formation of incandescent carbon at b , giving the lower visible flame front. When the particle reaches the point a , the luminous stage ends, and the molecules continue on into the upper zone and into the atmosphere.

Consider now gas molecules P_2 leaving the tip somewhat after P_1 . The first stages are exactly the same as before, but the luminous stage continues for a longer period of time, until the molecules reach the height k . Apparently the oxidation has taken place at a slower rate and allowed combustion to continue for a longer period. In the case of a particle P_3 the combustion stage continues still longer, but in the case of P_4 the active stage ends at m . Thus the distinction between the flame fronts AA and CC

is purely arbitrary, as they represent the same kind of a change from luminous to nonluminous. In the case of a particle P_5 the luminous stage not only ends at a lower point, but also ends before the corresponding change from P_4 . This point n is a critical one, for it is here that the flame divides into two portions, one giving the flame ending at g and the other being the main continuous flame. We have the peculiar phenomenon, then, of the main flame periodically giving off another minor flame.

Whether the end of the luminous stage is considered to be due to the lack of oxygen or of combustible gas, the periodic nature of the phenomenon is due to alternate decreases and increases in the rate of diffusion of oxygen into the flame. A slow rate of diffusion would be associated with the minima of flame heights, the high rate of diffusion with the maxima.

In that there is a flame-speed phenomenon in the envelope around the true flame, the passage of this flame upward and outward leaves the flame envelope covered with the products of the combustion. The flame is then seen in its original state, as there is a time interval before the slower moving air can diffuse through this envelope and again form an envelope of gas-air mixture that will inflame when it reaches its maximum limit of inflammability if it has attained its ignition point. As air diffusion is greater in the same time in the upper portion of the flame structure, the flame speed will be greater.

Acknowledgment

The authors are indebted to H. H. Romig, a senior student in chemical engineering in Lehigh University, for his help and study in obtaining and correlating these data.

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FLAME SPEED OF HYDROGEN SULFIDE

D. S. CHAMBERLIN AND D. R. CLARKE

Lehigh University, Bethlehem, Pennsylvania

An apparatus and method for determining the flame speed of hydrogen sulfide in air by horizontal flame propagation are described. The flame records were made by photographic method, the gas being inflamed in a 2.5-cm glass tube, open at one end and 1 meter long. The maximum flame speed was found to be 49.5 cm per second on burning 10.8 per cent hydrogen sulfide.

The various methods for the measurement of flame speeds are well understood as there has been a decided development in the experimental method starting with Bunsen in 1857. Mallard and LeChatelier¹ first applied the photographic method which was later developed by Dixon,² Bone,³ Wheeler,⁴ and other investigators. Little difficulty was met in the manipulation of the various combustible gases of which we have flame-speed data, as their solubilities and chemical activities were so low they could be easily measured and manipulated over water, aqueous solutions, or mercury.

Hydrogen sulfide, on the other hand, is readily soluble in aqueous solution, oils, mercury, and liquid organic compounds, and in many cases chemically combines with them. Nevertheless, Jones, Yant, and Berger⁵ determined the limits of inflammability of hydrogen sulfide and made quantitative measurements over saturated hydrogen sulfide water. Applebey and Lanyon⁶ explained a system for the generation, storage, and delivery of pure hydrogen sulfide over a saturated hydrogen sulfide solution. It was found that all the existing methods for the storage, manipulation, and quantitative determination of air-H₂S mixtures were so inaccurate that even approximate analyses could not be made. It was therefore necessary to develop a method for handling hydrogen sulfide in which it did not come in contact with liquids.

Apparatus and Materials

The apparatus used for the handling and analysis of the H₂S-air mixtures, shown in Fig. 1, consists essentially of gas-measuring pipets *s* and

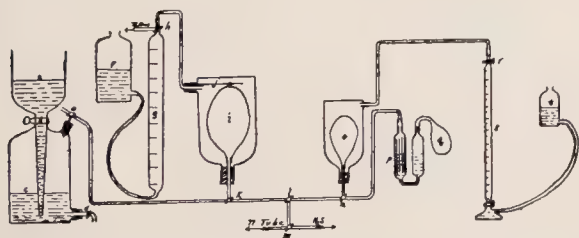


FIG. 1. Apparatus for collecting and analyzing mixtures of H₂S and air.

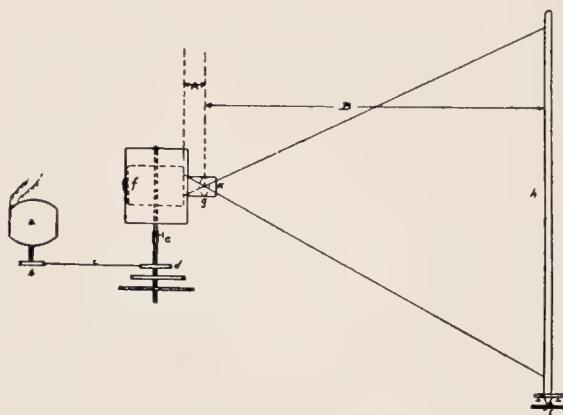


FIG. 2. Apparatus for determining speed of flames.

g, absorption tube *p*, and balloons *i* and *o* for containing the H₂S-air mixtures.

Figure 2 shows the flame speed set-up similar to others in use.⁷ A constant speed motor, *a*, drives a cone drive, *d*. This is connected to a drum carrying film *f* in the camera box. The lens is at *g* and the flame tube in the proper focus at *l*. The flame tube is 1 meter long and 2.5 cm internal diameter. A vacuum-tight removable end holds a three-way stopcock for evacuating and filling the tube with proper mixtures.

Hydrogen sulfide containing a trace of air was used from pressure cylinders as obtained from the Mathieson Alkali Company. The air was contained in a reservoir over water at 25°C and slightly above atmospheric pressure.

Experimental Method

The limits of inflammability of H₂S-air mixtures by horizontal propagation with one end of the tube open are as follows:

Tube diameter, cm.	Limits, %
7.5	5.3 to 35.0
6.0	5.9 to 27.2

From the data one can assume that the limits of inflammability in a 2.5-cm. diameter tube would be within the above limits.

Manipulation. A small hydrogen sulfide cylinder of compressed gas was connected to cock *m*

TABLE I
Flame speed—H₂S—air mixtures

H ₂ S, %	Flame speed, cm/sec	H ₂ S, %	Flame speed, cm/sec
7.5	16.0	10.0	49.5
8.0	40.1	12.2	48.0
8.9	45.8	12.5	40.1
9.0	46.5	16.2	26.4
9.5	48.0	20.0	24.0

(Fig. 1). The circuit *e, i, k, l, m, n, o*, was evacuated with cocks *h* and *r* open to the atmosphere. Cock *h* was then turned to communicate with the 1-liter pipet *g*, and hydrogen sulfide allowed to flow through *k* into the dry rubber bag *i*. Air was then run in from reservoir *c* through *e* to the bag *i*, and the air displaced by the added inflation of the bag was measured at *g*. In this way a rough mixture of hydrogen sulfide and air was made. By alternately raising and lowering the leveling bottles *f* and *t* with communicating cocks open, the gases were well mixed.

Analysis. In order to obtain an exact analysis of the mixture, a sample of the gas from *i* was run into the small gas bag *o* and the volume accurately measured by air-water displacement in pipet *s*. By turning the cock *n* to communicate with the gas-absorption pipet *p*, the contents of *o* can be forced into a 10 per cent solution of ammoniacal cadmium chloride.

After analysis the completely evacuated flame tube was attached to *m* and the gas mixture in *i* expanded into the tube. The residual gas in *i* was again sampled into *o* and a check analysis run.

Measurement of Flame Propagation. The photographic method by which the uniform propagation of the hydrogen sulfate flame was measured was carried out by a method similar to those previously mentioned. The flame tube of a capacity of 464 cc was ignited from the open end by a taper. Immediately after the inflammation the tube was closed so that the products of the

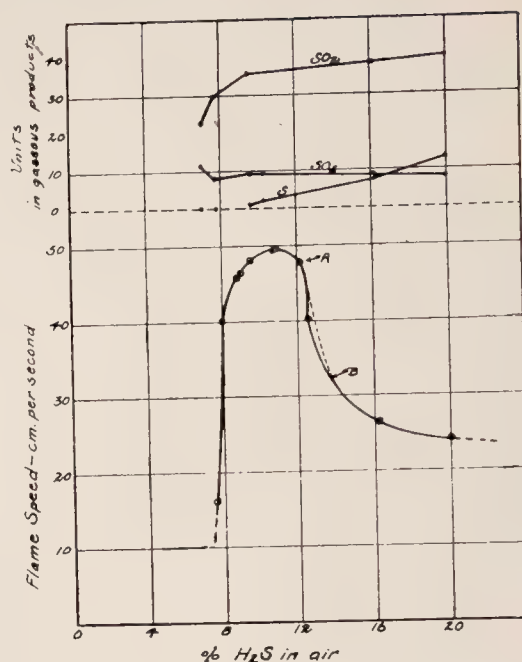


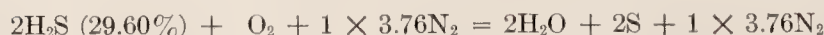
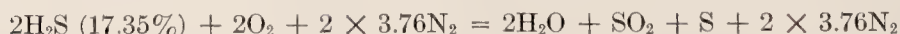
FIG. 3. Flame-speed curves for H₂S—air mixtures by horizontal flame propagation.

combustion could be investigated. The film used to obtain the flame speed record was 4 5/16 inches (11 cm) wide and 20 inches (50.8 cm) long.

The constant factors were the focal length of the lens and the distance of the lens from the flame tube. The variables were the speed of the film as measured by the rpm of the drum and the angle formed by the image of the moving flame on the film. From these data the speed of the flame in centimeters per second was easily obtained.

Results and Discussion

The values for the flame speed of H₂S—air mixtures are shown in Table I and plotted in Fig. 3. The curve conforms very closely to the flame-speed curves for other combustible gases but differs in some detail. The fact that the sulfur in hydrogen sulfide can be oxidized, as follows, from $S^{--} \rightarrow S^{\circ} \rightarrow S^{++} \rightarrow S^{+++}$, indicates that the following reactions can express the conditions that give rise to flame speeds with proportions of hydrogen sulfide in air within its limits of inflammation:



From actual analyses of the gases in the flame tube resulting from the combustion, the plots of the amounts of S_2 , SO_2 , and SO_3 , corresponding with the same abscissas as in Fig. 3, show that the hydrogen is to a great extent selectively oxidized. This fact was also noted in that gas mixtures that contained percentages of hydrogen sulfide above 12.3 per cent, showed poorer images on the film due to the increasing amount of hydrogen burned and the formation of greater amounts of sulfur. It is well known that the flame speed of hydrogen cannot be determined in the time allowable by photographic method due to the fact that the light rays that are given off are in the ultraviolet and do not affect the photographic film rapidly.

Between the points *A* and *B*, if no sulfur had been deposited and only sulfur dioxide formed, the curve would no doubt have conformed to its proper shape as shown by the dotted line and the flame speed not abruptly retarded by the formation of suspended sulfur.

It is interesting to note that the slowest maximum flame speed heretofore measured was that of carbon monoxide in air in a 2.5-cm tube and

found to be 60.0 cm per second. It is now evident that hydrogen sulfide at its maximum flame speed of about 50.0 cm per second moves much slower than carbon monoxide and thus will affect the burning of combustible gases containing hydrogen sulfide.

In these experiments the sulfur trioxide content of the gases of combustion was at a maximum on igniting a 7.0 per cent mixture of hydrogen sulfide in air. A continuous method for the production of sulfur trioxide by burning hydrogen sulfide in an internal-combustion engine warrants further study.

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THE GASEOUS EXPLOSIVE REACTION AT CONSTANT PRESSURE*

F. W. STEVENS

Bureau of Standards, Washington, D. C.

The course of the gaseous explosive reaction at constant pressure is described and then followed experimentally by means of photographic time-volume records obtained by a simple device that is found to function as a transparent bomb of constant pressure. It is found that at constant pressure the uniform rate of propagation, s , of the zone of explosive reaction, when measured relative to the active gases, is proportional to the product of their concentrations (partial pressures):

$$s = k_1 [A]^{n_1} [B]^{n_2} [C]^{n_3} \dots$$

In the light of this relationship studies have been made of the effect of inert gases and of composite fuels on the rate of the gaseous explosive transformation.

Nearly all the investigations that have been made of the gaseous explosive reaction have been carried out under conditions of constant volume. This has seemed necessary from the very nature of gases. Of all these investigations, those that show some connection with the line of substantial development taken by our knowledge of gaseous transformations, and that have sought the direction for further advance indicated by well-established general principles and laws, have been devoted to thermodynamic studies of the reaction and have concerned themselves principally with gaseous equilibria. The significant advance that has resulted from such studies must be attributed in large measure to the fact that they took advantage of the leadership and direction provided by the theoretical consequences involved in the principles and laws of thermodynamics as applied to chemical equilibria. These deductions were early (1876) set forth in the far-reaching theoretical investigations of Gibbs. As a result of his work "chemical science has been able to use these results of theoretical physics with immense benefit to itself and to deal quantitatively with the most complex equilibria without any knowledge of the intimate 'mechanisms' underlying physical and chemical phenomena."¹

On the other hand, kinetic studies of the gaseous explosive reaction made under conditions similar to those imposed for thermodynamic investigations have not shown a corresponding advance. As compared with thermodynamic studies, the number devoted to the kinetics of the reaction and based in any way upon or directed by the probable consequences of a kinetic theory of gases are few; yet for the kinetic phase of the reaction the opportunity has long been at hand to adapt experimental devices and methods to the principles of statistical mechanics. Even

with a primitive kinetic theory, early attempts in this direction met with significant success: "The first attempt at a quantitative kinetic expression is met with in the equation $pV = RT$."² Very early also (1864) "the assumed correspondence between the order and mechanism (of a reaction) which finds its rational explanation on the basis of a kinetic theory of molecular motions, was, of course, the original hypothesis of Guldberg and Waage in the formulation of the law of mass action.* * * The rational procedure seems to be to regard the order of any simple reaction as *prima facie* evidence of its mechanism."³

The advance in physics of late years has been somewhat diverted from the physics of large aggregates to the physics of individuals, thus depending for a prediction of the behavior of the mass on the behavior of an isolated individual. The direction taken by this more recent development is said "to hold out the hope that the time will come, perhaps in no very distant future, when the structure and activity of the material world will be understood in terms of a theory based on the potentialities and activities of electrons, protons and radiation, or possibly of radiation alone. Although such a theory already exists, it is not sufficiently developed to suffice for the needs of the chemist,"¹ whose problems are for the most part concerned with systems, often of great complexity.

"Among the immediate developments to be wished for statistical mechanics will be its increasing applications to systems. * * * The problem of reaction velocity is probably nearer the heart of most chemists than anything else in their whole range of activity. Rates of reaction are the factors that determine yields and costs, and possibilities and their theory must eventually succumb to scientific treatment."⁴

In the present paper are offered some results obtained in a study of gaseous explosive reactions at constant pressure. Since these reactions are confined to the gaseous state, they can never be

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freed entirely from hydrodynamic disturbances set up in the gaseous fluid by the explosive reaction itself. These disturbances, affecting the concentrations of the active gases and their mass movement, are much more profound when the reaction takes place under conditions of constant volume than they are under conditions of constant pressure. Under the latter conditions the gross mechanism of the explosive reaction—the spatial propagation of a sharply defined reaction zone within the gases—may assume a form of nearly perfect symmetry and a uniform rate of propagation. This simplification, secured by constant-pressure methods, is essential to kinetic studies of the reaction and advantageous also to thermodynamic investigations. The relation between the thermodynamic results obtained at constant pressure and those resulting from conditions of constant volume is expressed by the equation of state,

$$pv = nRT. \quad (1)$$

The direction taken by the studies here offered has been influenced largely by the known order of reactions studied. The kinetic principles applied to them are primitive and simple.

Characteristics of Gaseous Explosive Reaction

A most important characteristic of the gaseous explosive reaction was early established by the investigations of Bunsen⁵ of Gouy,⁶ and of Michelson.⁷ It was to the effect that the movement of the zone of explosive reaction within a homogeneous mixture of explosive gases is constant under conditions of constant pressure, and independent of the mass movement of the active gases in which it is propagated. This result has for years found extensive practical application in those numerous cases where a homogeneous mixture of explosive gases is fed through a tube at a constant time-volume rate and ignited. The zone of continuous explosive reaction automatically adjusts itself under these conditions so that its linear rate of advance measured relative to the active gases is a constant, s , at any point of the flame surface. If this were not the case, the many industrial devices based on the gaseous explosive reaction as controlled by some form of burner would not be practical. This characteristic as expressed by the investigators mentioned may be written

$$s = v_p/ta, \quad (2)$$

where v_p is the volume at constant pressure passing unit element of the flame surface, a , in time t .

When this principle is applied to ideal conditions where the homogeneous mixture of explosive gases may be conceived as existing at rest and unconfined in space, and the explosive reaction started at some point within the mixture, then, s being constant, it should be found that the zone of explosive reaction originating at the point of ignition should propagate itself in all directions from this point at uniform rate at constant pressure. The reaction zone should thus assume the form of a spherical shell of flame expanding at a uniform linear rate, s' , in space. This rate in space, s' , is the linear rate s at which reaction zone is entering the explosive gases, plus the constant rate at which the gases are being moved outward against the static pressure of the surroundings, p_0 . The constant pressure, p_1 , then, at which the reaction takes place under these conditions, is not p_0 , but p_0 plus the pressure necessary to produce the observed rate of movement, s' , in space. That is,

$$p_1 = p_0 + \frac{1}{2}(\rho s'^2), \quad (3)$$

where ρ is the density of the gases.

Since the rate of pressure distribution in the gaseous system is limited to the rate at which sound is propagated in the gases, it will be seen that as long as the value of s' does not approach too near the velocity of sound in the gases, the value of the last term in Eq. (3) is small and may be negligible. But for values of s' above that of sound in the gases, it becomes the more important factor, since under these circumstances, as Hugoniot⁸ has shown, the law of static adiabatics no longer applies; the pressure in the thin impact wave at the seat of reaction increases for velocities above that of sound much more rapidly than the square of s' . It is, therefore, the pressure at the seat of reaction, and not that indicated at some point more or less remote, that should be considered in determining the pressure conditions of the reaction and its effect upon reaction rate.

Applying the law of Hugoniot instead of the simple impact expression given in Eq. (3), Chapman,⁹ Jouguet,¹⁰ Crussard,¹¹ and Becker¹² have made extended analyses of the impact pressure conditions accompanying the flame when its velocity of propagation exceeds that of sound in the gases, and when, in consequence, the course of the reaction becomes independent of a container. These constant-pressure conditions apply to the high rates of flame propagation met in the Berthelot explosive wave,¹³ sometimes called detonation, where the reaction runs its course under conditions of a constant pressure of many atmospheres. The flame velocity under these conditions of constant impact pressure is found, as in the case of much lower constant

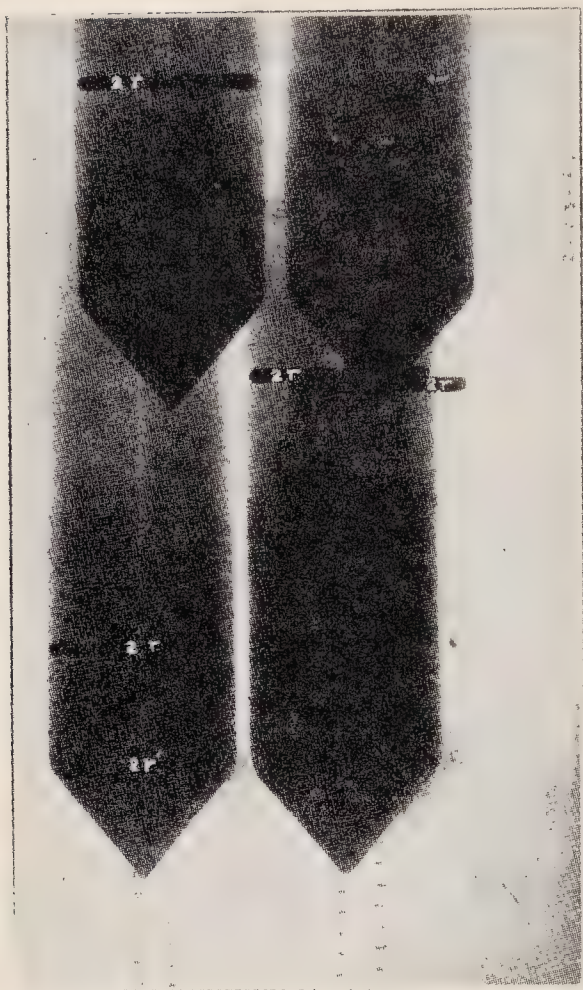


FIGURE 1
(One-tenth actual size)

pressures dealt with in this paper, to be strictly constant.

The conditions that determine uniform flame movement in a gaseous explosive reaction, whether for the slower reaction rates or for the more rapid rates of the explosive wave, are a homogeneous mixture of the explosive gases and a constant pressure during their transformation; for under these conditions only it is possible for the mass movement of the active gases and for their concentrations to remain constant during the reaction process.

These ideal conditions, under which the gaseous explosive reaction might run its course at a constant pressure, unconfined in space, may be closely realized in practice by enclosing temporarily the homogeneous mixture of explosive gases in a soap film and firing the mixture from the center. Figure 1 is a photographic reproduction of a time-volume record of four gaseous explosive reactions of the same initial composition obtained by such a device.¹⁴ This simple arrangement is found to function as a bomb of constant pressure. It thus forms the complement to the

bomb of constant volume. The diagram in Fig. 2 may assist in pointing out this relationship: A silhouette of the bubble giving its horizontal diameter, $2r$, through the spark gap is secured while the photographic film is at rest. Since the photographs are made to scale, this figure gives the actual diameter of the sphere of active components whose transformation is to be followed. The photographic film is then set in rapid motion and an ignition spark passed. An image, a , of the spark is obtained on the moving film near the time record, $t-t$, from a calibrated fork. The point a marks the center of the expanding spherical zone of reaction. Only its horizontal motion outward from this point, and perpendicular to the direction of motion of the photographic film, is recorded. The flame trace on the film is thus the resultant of the vertical known rate of motion of the photographic film and the horizontal motion of the zone of reaction. That its motion, under the constant-pressure conditions afforded by a soap-film bomb of constant pressure, is constant is indicated by the right line, ab , made by its trace. The slant of this line gives the rate of motion of the reaction zone in space. As the figures show, this rate in space, s' , may be determined at any instant during the reaction. It is equal to the radius of the reaction zone at any instant, r_i , divided by the time interval, t , between ignition and the attainment of r_i :

$$s' = r_i/t. \quad (4)$$

But this rate in space is not the rate at which the

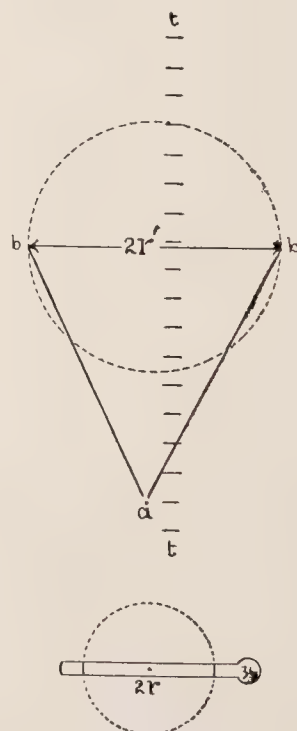


FIGURE 2

reaction zone is entering the active gases and effecting their transformation independent of their mass movement. The velocity, s , of the reaction zone, measured relative to the active gases it is entering is given for the case where the zone is an expanding spherical shell of flame, by

$$s = v_p/ta = s' (r^3/r'^3), \quad (5)$$

where r and r' represent the initial and final volumes of the reacting gases considered.

If the rate of movement of the reaction zone is to be connected in any way with the rate of molecular transformation of the explosive gaseous system, and hence with the rate of energy liberation, it is obvious that its rate should be determined relative to the gases it is transforming and not relative to space. It is also clear that unless the method employed makes it possible to follow the concentrations (partial pressures) of the active gases the zone of explosive reaction is entering, a kinetic relation connecting the movement of the reaction zone with the composition and concentrations of the explosive gases could hardly result. Such a relationship, however, is suggested by a number of considerations. Haber¹⁵ has pointed out that in the progress of a gaseous explosion the gaseous system automatically falls into three well-defined zones. These three zones, in the case of a constant-pressure bomb, maintain a symmetrical position about the point of ignition throughout the reaction process. He designates these zones as (1), the region occupied by the explosive gases, (2) the zone of explosive reaction marked by flame, (3) the region occupied by the equilibrium products behind the flame. This latter region, he states, "is not from a thermodynamic standpoint free from oxygen, but from an analytical standpoint it is; in this region no further burning takes place." It is a region of chemical equilibrium depending on temperature and pressure and defined by the equilibrium constant,

$$K = \frac{[A']^{n'_1} [B']^{n'_2} [C']^{n'_3} \dots}{[A]^{n_1} [B]^{n_2} [C]^{n_3} \dots} \quad (6)$$

The kinetic relation leading to the above equilibrium expression is written for the rate of molecular transformation,

$$V = k [A]^{n_1} [B]^{n_2} [C]^{n_3} \dots - k' [A']^{n'_1} [B']^{n'_2} [C']^{n'_3} \dots \quad (7)$$

The experimental application of the above-formulated principles may be best illustrated by a particular case to which they have been applied—viz., to the gaseous reaction



Since the equilibrium condition of a reaction for a given temperature and pressure is independent of the way by which it is attained, it may be assumed that the course of this trimolecular transformation within the zone of explosive reaction is described by the relation

$$V = k [\text{CO}]^2 [\text{O}_2] - k' [\text{CO}_2]^2 \quad (9)$$

and that the equilibrium condition of the process is expressed by

$$K = \frac{[\text{CO}_2]^2}{[\text{CO}]^2 [\text{O}_2]} \quad (10)$$

Should the reaction proceed almost wholly in one direction, as is usually the case in explosive reactions of gases, the last term in Eq. (9) may be neglected¹⁶ and the kinetic expression for the molecular rate of transformation written

$$V = k [\text{CO}]^2 [\text{O}_2]. \quad (11)$$

If, now, by some means the successive concentrations of carbon monoxide and oxygen during the period of transformation from their initial to their final condition could be maintained constant by the introduction into the reaction zone of new initial components *at the same rate* that the reaction products are removed from the reaction zone to the equilibrium zone, then the zone of explosive reaction would represent a constant reaction gradient across it, and the relative rate of motion, s , between the reaction zone and the initial gaseous components would remain constant and s would express the gross rate at which equilibrium was being established in the gaseous system.

But this imagined process of supplying initial active components to a reaction zone *at the same rate* that the equilibrium products are removed—an analytical device first made use of by van't Hoff¹⁷—is automatically carried out wherever a gaseous explosive reaction is so conditioned that it may run its course in a homogeneous mixture of explosive gases at a constant pressure. Observation shows that under these conditions the rate of propagation, s , of the zone of explosive reaction, measured relative to the initial active gases, remains constant during the reaction.

Since the rate of molecular transformation at any instant between the initial and end conditions of the reaction process remains proportional to the product of the concentrations of the active gases, it was assumed that s , analogous to V , would sustain a like relation to the composition of the explosive gases, the initial concentrations of which may be known:

$$s = k [\text{CO}]^2 [\text{O}_2]. \quad (12)$$

TABLE I

Rate of flame propagation in 2CO + O₂ explosive reaction at constant pressure

Record 9-7-27 No.	Partial pressure		$\Gamma = [\text{CO}]^2[\text{O}_2]$	$s' = r_i/t$	$s = s'(r^3/r'^3)$	$k_1 = s/\Gamma$
	[CO]	[O ₂]				
	atm	atm		cm/sec	cm/sec	
1 to 3	0.224	0.776	0.0389	191	27.6	709
4 to 7	0.260	0.740	0.0500	226	34.7	694
8 to 11	0.279	0.721	0.0561	279	37.5	668
12 to 15	0.310	0.690	0.0663	335	45.3	683
16 to 19	0.325	0.675	0.0713	365	50.3	705
20 to 23	0.359	0.641	0.0826	434	55.5	672
24 to 27	0.388	0.612	0.0921	487	63.3	687
28 to 31	0.416	0.584	0.1011	561	71.1	703
32 to 35	0.460	0.540	0.1140	632	80.3	703
36 to 39	0.491	0.509	0.1227	660	84.3	687
40 to 43	0.523	0.477	0.1305	715	88.4	678
44 to 47	0.574	0.426	0.1404	794	99.8	711
48 to 51	0.622	0.378	0.1463	858	100.6	688
52 to 55	0.688	0.332	0.1480	870	102.8	694
56 to 59	0.726	0.274	0.1444	849	101.9	706
60 to 63	0.775	0.225	0.1351	814	92.2	682
64 to 67	0.810	0.190	0.1247	733	86.4	693
68 to 71	0.840	0.160	0.1129	632	79.2	701
72 to 75	0.848	0.152	0.1093	614	77.7	711
76 to 79	0.883	0.117	0.0912	463	63.9	700
80 to 83	0.903	0.097	0.0791	320	50.1	633

Av. 691

Including Eq. (5)

$$s = s' (r^3/r'^3) = k [\text{CO}]^2 [\text{O}_2], \tag{13}$$

and since the method employed determines *s* directly,

$$k = \frac{r^3}{r'^2 t [\text{CO}]^2 [\text{O}_2]}. \tag{14}$$

In Table I are set down the experimental results obtained from the photographic records of the explosive reaction 2CO + O₂ →. These results cover the range of mixture ratios of [CO] and [O₂] that will support a zone of explosive reaction. Figure 3 illustrates graphically the relation between the rate of propagation, *s*, of the reaction zone and impact probability,

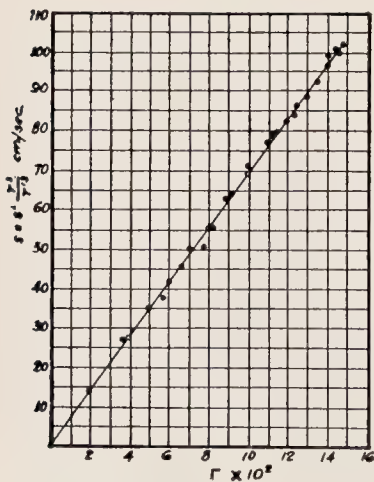


FIGURE 3

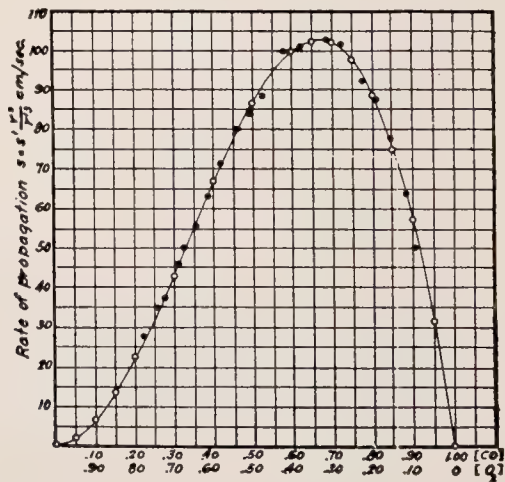


FIGURE 4

$\Gamma = [\text{CO}]^2 [\text{O}_2]$, for this order of reaction. Figure 4 illustrates the more familiar relationship between rate of propagation, s , and the partial pressures of the active gases. Solid circles represent observed values, $s = s' (r^3/r'^3)$; the open circles and continuous line represent calculated values, $s = k [\text{CO}]^2 [\text{O}_2]$.

Effect of Inert Gases

The effect of inert gases on the thermodynamic equilibrium of gaseous explosive reactions has received extensive consideration both from experimental and theoretical standpoints. This series of investigations,¹⁸ in which a spherical bomb of constant volume with central ignition was used, formed a part of the most extensive investigation of gaseous reactions involving the equilibrium products of combustion, carbon dioxide and water vapor, that has yet been carried out. "No other chemical equilibrium has so far been investigated by so many methods which can also be controlled at the same time by thermodynamic calculation.* * * A specially high value must be attached to explosion methods since, by suitable variations of the experimental conditions, it enables both the specific heats and the equilibrium to be determined."¹⁹

It was of interest to examine the effect of inert gases on the rate of propagation of the zone of reaction in the light of the statistical relation expressed in (12); and, by a method suggested by that employed by the investigators, mentioned above, in determining the effect of inert gases upon the thermodynamic equilibrium (6) and the degree of dissociation of combustion products.

Since the sum of the partial pressures of the gaseous components present in the reaction at pressure p must equal p , Eq. (12) may be written for atmospheric pressure,

$$s = k [\text{CO}]^2 [1 - \text{CO}] \quad (15)$$

without designating the composition of the factor $[1 - \text{CO}]$ further than to indicate that the sum of the partial pressures of its components remains the same as the partial pressure of the factor $[\text{O}_2]$ in Eq. (12); and that under the same conditions both expressions, $[\text{CO}]^2 [\text{O}_2]$ and $[\text{CO}]^2 [1 - \text{CO}]$, represent the same impact probability, Γ , though not the same proportion of favorable impacts nor the same potential energy. In case the component $[1 - \text{CO}]$ is made up of the fraction a of the active gas O_2 and the fraction $1 - a$ of an inert gas, the partial pressure of this component may be expressed as

$$[1 - \text{CO}] = \underbrace{[1 - \text{CO}]a}_{\text{active}} + \underbrace{[1 - \text{CO}] (1 - a)}_{\text{inert}} \quad (16)$$

Equation (15) may then be written

$$s = k_1 [\text{CO}]^2 [1 - \text{CO}]a + k_1 [\text{CO}]^2 [1 - \text{CO}] (1 - a). \quad (17)$$

Should all of the impacts involving the inert gas be futile and the possible effect of its various physical properties, as molecular heat, heat conductivity, etc., on the course of the reaction be disregarded, then the last term in Eq. (17) may be neglected and the effect on reaction probability of replacing the fraction $(1 - a)$ of an active gas by an inactive one be written

$$s = k [\text{CO}]^2 [1 - \text{CO}]a. \quad (18)$$

This expression takes into account the effect of the remaining active components only, and this is the major effect to be expected; but while the inert gas introduced may take no part in the molecular transformation, its presence in the zone of explosive reaction and in the active gases adjacent to it would naturally affect the heat distribution in that region. The effect of different inert gases upon the thermodynamic equilibrium is not the same; a quantitative estimate of their different effects permits their specific heats to be determined under the conditions resulting from the explosive reaction of the known active gases. It might therefore be expected that the presence of inert gases in the zone of reaction would likewise have different effects upon the propagation of the reaction zone due to their individual characteristics.

In carrying out the observations on the effect of inert gases, the experiments were so arranged that the explosive transformation of the same partial pressures of the active gases, carbon monoxide and oxygen, could be observed on the same partial pressure of each of the inert gases

TABLE II
Molecular heats and heat conductivities
of gases studied

Gas	Molecular heat ^a	Heat conductivity ^b
Helium	5.07	336.0
Argon	5.07	39.0
Nitrogen	6.90	56.6
Oxygen	6.90	57.0
Carbon monoxide	6.90	54.2
Carbon dioxide	9.00	33.7

^a PARTINGTON and SCHILLING: "Specific Heat of Gases."

^b TAYLOR: "Treatise on Physical Chemistry," Vol. I, p. 92.

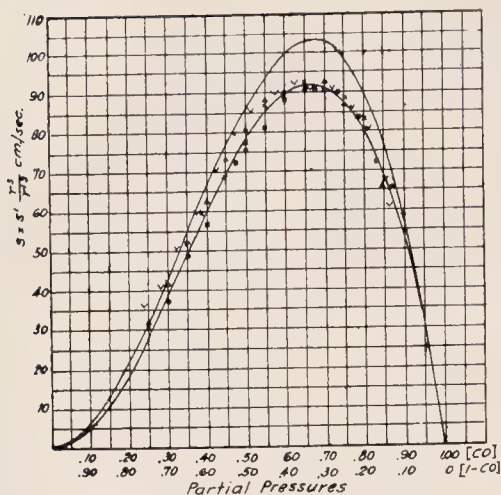


FIGURE 5

used, and this over the entire range of mixture ratios of the gases that would ignite. The inert gases made use of were helium, argon, nitrogen, and carbon dioxide. Table II gives some of the physical properties of the gases involved in the transformations studied.

Figure 5 shows graphically the experimental values of $s = s' (r^3/r'^3)$ when 10 per cent of the component $[1 - \text{CO}]$ consisted of an inert gas. The values for helium are indicated on the figure by the solid triangle; those for nitrogen by (x); those for carbon dioxide by the solid square; and those for A by (v). The same system of marks will be used for these gases in the other figures to be given. The upper continuous curve in this figure indicates values of s for the $\text{CO}-\text{O}_2$ reaction when no inert gas is present. It is the curve given in Fig. 4 and is reproduced here as a convenient reference. The lower continuous curve corresponds to Eq. (18), $s = 691 [\text{CO}]^2 [1 - \text{CO}]^{0.9}$. It is the theoretical locus of s values on the assumption that the inert gases

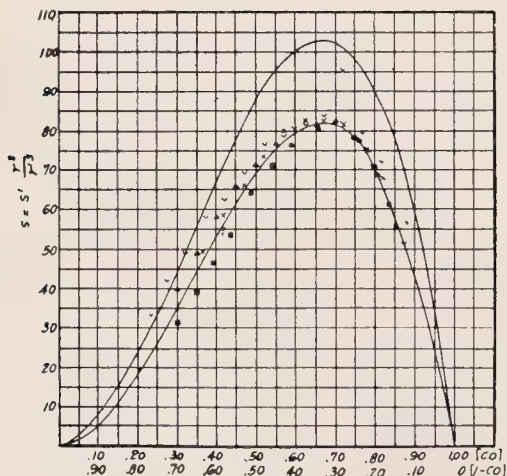


FIGURE 6

have no effect whatever on the reaction. In this case the observed values with all the inert gases agree fairly well with this theoretical curve.

Figure 6 shows experimental results obtained when 20 per cent of the component $[1 - \text{CO}]$ consisted of an inert gas. The upper continuous curve in this figure again represents the locus of s values when no inert gas is present. The lower continuous curve corresponds to Eq. (18) for this case: $s = 691 [\text{CO}]^2 [1 - \text{CO}]^{0.8}$.

In Fig. 7 are shown the experimental results obtained when 40 per cent of the component $[1 - \text{CO}]$ consisted of an inert gas. The upper continuous curve corresponds to Eq. (12) when no inert gas is present, $s = 691 [\text{CO}]^2 [\text{O}_2]$. The lower continuous curve corresponds to Eq. (18) for this case: $s = 691 [\text{CO}]^2 [1 - \text{CO}]^{0.6}$.

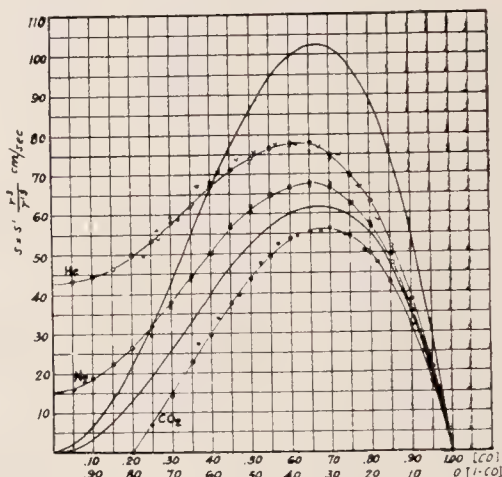


FIGURE 7

To illustrate how all the results are tabulated, the results with helium are given in Table III. From these results and from the coordinate figures given it may be seen that when small amounts (partial pressures) of different inert gases are present in the explosive mixture, there is not much difference in their individual effects; their different physical properties do not mask the effect of the active gases, but, as the relative amounts (partial pressures) of the inert gases become greater and the partial pressures of the active gases less, a difference in their effect on the same $\text{CO}-\text{O}_2$ reaction becomes apparent (Fig. 7). The observed s values not only diverge more widely from values indicated by Eq. (18), but they also differ characteristically from each other. It is further to be noticed that this divergence in each case is the greater the greater the amount (partial pressure) of inert gas in the mixture. In column 4, Table III, is given the partial pressure of He in each mixture ratio of $[\text{CO}]$ and $[1 - \text{CO}]$. In column 8 of this table are

TABLE III
Results obtained when 40 per cent of component [1 — CO] consisted of helium

2-5-27 No.	Partial pressure			$\Gamma = [\text{CO}]^2 [1 - \text{CO}]$	$s' = r_i/t$	$s = s'(r^3/r'^3)$	$k_1 = s/\Gamma$	$\beta = \frac{s - k_1 a [\text{CO}]^2 [1 - \text{CO}]}{[\text{He}]}$
	[CO]	[1 - CO]	[He]					
	atm	atm	atm		cm/sec	cm/sec		
8' to 11'	0.217	0.783	0.313	0.0369	262	49.5	1342	109
5' to 8'	0.265	0.735	0.294	0.0516	339	56.1	1088	118
4 to 7	0.302	0.698	0.279	0.0637	376	59.9	940	120
8 to 11	0.351	0.649	0.260	0.0811	449	61.4	757	107
12 to 15	0.400	0.600	0.240	0.0960	498	68.0	708	117
16 to 19	0.450	0.550	0.220	0.1114	541	71.8	645	116
20 to 23	0.500	0.500	0.200	0.1251	567	72.3	578	102
24 to 27	0.550	0.450	0.180	0.1362	631	75.8	557	107
28 to 31	0.600	0.400	0.160	0.1441	613	76.5	531	105
32 to 35	0.650	0.350	0.140	0.1479	612	76.6	518	114
36 to 39	0.700	0.300	0.120	0.1470	591	73.9	503	108
40 to 43	0.750	0.250	0.100	0.1406	538	69.5	506	112
44 to 47	0.800	0.200	0.080	0.1280	446	61.3	479	102
48 to 51	0.850	0.150	0.060	0.1084	298	51.0	471	101

Av. 109

given the corresponding values of $k_1 = s/\Gamma$. The values of k_1 in this column, according to Eq. (18), should be a fair constant and equal to 415 if the inert gas was without effect. The values of k_1 are seen to be far from constant in this case and only approach the theoretical value as the partial pressure of helium in the mixture decreases. The highest value of k_1 is seen to correspond to the greatest amount of helium in the explosive mixture, and vice versa.

Having in mind the method by which the effect of inert gases on the thermodynamic equilibrium was determined, it was conceived that the relationship shown in the table between the values of k_1 and $[\text{He}]$ could be due to characteristic physical properties, whatever they might be, of the inert gas present in the mixture, and that the magnitude of their different effects upon the CO-O_2 reaction might be directly proportional to the partial pressure of the inert gas in the mixture. That is,

$$s = s'(r^3/r'^3) = k_1 [\text{CO}]^2 [1 - \text{CO}]a + \beta[G_i], \quad (19)$$

where $[G_i]$ is the partial pressure of the inert gas and β a proportionality factor. The observed results were examined for this relationship. The last column of Table III gives the estimated value of β for each mixture ratio of $[\text{CO}]$ and $[1 - \text{CO}]$ that would support a zone of reaction

$$\beta = \frac{s - (k_1 a [\text{CO}]^2 [1 - \text{CO}])}{[\text{He}]} \quad (20)$$

When the average value of β so found, 109, is substituted in Eq. (19), the curve represented by open circles and a continuous line, marked He in Fig. 7 is determined. In a similar way it was found that the value of β for each of the other inert gases used was also a fair constant. Its value for 40 per cent nitrogen in this reaction is 41, for carbon dioxide, -41.8, and for argon, 112. Helium and argon are both monatomic gases and hence have the same molecular heat independent of temperature. But their heat conductivities vary greatly. Both gases have practically the same effect on the s values of the CO-O_2 explosive reaction. It is of interest to compare the relations shown by the coordinate figures with the table giving some of the physical properties of the gases involved in the different reactions.

Some Observations on a Study of a Composite Fuel

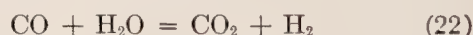
In the practical application of the gaseous explosive reaction as a source of power in the gas engine, the fuels employed are composite, with characteristics that are likely to be due to the characteristics of their components and hence

may be somewhat complex. The simplest problem that could be proposed in an investigation either of the thermodynamics or kinetics of the gaseous explosive reaction of a composite fuel would seem to be a separate study of the reaction characteristics of each component of the fuel and then a study of the reaction characteristics of the various known mixtures of those components forming composite fuels more and more complex. This is the order followed in the simple study to be described.

Whether a simple gas is used or a mixture of a number of simple gases, or a gaseous fuel of quite unknown composition, the gross mechanism of the gaseous explosive reaction remains the same. The photographic records of the reaction at constant pressure differ in no way from those shown in Fig. 1. There is but one zone of explosive reaction in any case. Its rate of propagation is constant at constant pressure and its value may be expressed by

$$s = s'(r^3/r'^3) = k_1 [\text{F}]^{n_1} [\text{O}_2]^{n_2}. \quad (21)$$

Within the reaction zone the explosive gases proceed to an equilibrium condition of reaction products, however complex, K . The CO-O_2 explosive reaction here used as a typical example of a third-order transformation is not supposed to be as simple as indicated by the conventional chemical equation. The actual transformation is believed to depend upon intermediate reactions—at least for moderate initial temperatures and pressures. The reaction is supposed to involve an active catalyst, water vapor, and to proceed within the reaction zone as follows²⁰:



yet experimental thermodynamic and kinetic results reveal only the final condition of the reaction as if it had been simply trimolecular with normal maximum for such a reaction,

$$s = 691 \frac{[\text{CO}]^{0.667} [\text{O}_2]^{0.333}}{[\text{CO}] [\text{O}_2]} \quad (24)$$

The actual micro-process by which the equilibrium K is established within the reaction zone cannot be expected to be revealed by a method that takes into account the gross rate only at which an equilibrium condition is attained—that is, the rate at which the pressure at constant volume or the volume at constant pressure increases. The micro-transformation within the reaction zone may be very complex or comparatively simple; any knowledge of the actual process of it is limited by the present method to what may be drawn from a knowledge of the

initial and final conditions of the transformation, and its gross rate of progress. For instance, in the case under consideration some insight may be obtained concerning the effect of the amount of water vapor in the initial components upon the rate of propagation of the reaction zone. Drying the gases to a degree below saturation greatly diminishes the value of the velocity constant, k_1 . If the gases are dried as much as possible, they will no longer support a zone of explosive reaction at ordinary initial temperatures and pressures.

The fact that the probable intermediate reaction in the case of the CO-O₂ explosive transformation affected only the rate of propagation by its effect on k_1 suggested the possibility that the effect of composite fuels on the rate of propagation might be investigated with some success by the constant pressure method.

Composite fuels, that will be designated by F, were made up of carbon monoxide and methane in the known proportions given in Table IV. The characteristics of the explosive reaction of each of the above combinations designated by F were determined over the entire range of mixture ratios of F and O₂ that would ignite and the results tabulated and plotted. Sample records of the results obtained in this study, involving the measurement and calculation of many hundred explosion figures similar to those shown in Fig. 1, will be given for those combinations marked (*) in Table IV.

TABLE IV

Composition of Fuel F; observed and calculated values of k_F and composition of F and O₂ for maximum flame velocity, s

Partial pressures in fuel mixtures, F		Partial pressures for s maximum		k_F	
[CO]	[CH ₄]	[F]	[O ₂]	Obs.	Calc.
atm	atm	atm	atm		
*1.00	00	0.667	0.333	694	...
*0.95	0.05	0.637	0.363	1103	1051
0.90	0.10	0.625	0.375	1483	1364
0.80	0.20	0.557	0.443	2054	1927
0.70	0.30	0.513	0.487	2476	2412
0.60	0.40	0.476	0.524	2899	2829
*0.50	0.50	0.444	0.556	3180	3189
0.40	0.60	0.417	0.583	3505	3491
0.30	0.70	0.393	0.607	3794	3775
0.20	0.80	0.370	0.630	4034	4031
0.10	0.90	0.351	0.649	4177	4240
*0.00	1.00	0.333	0.667	4250	...

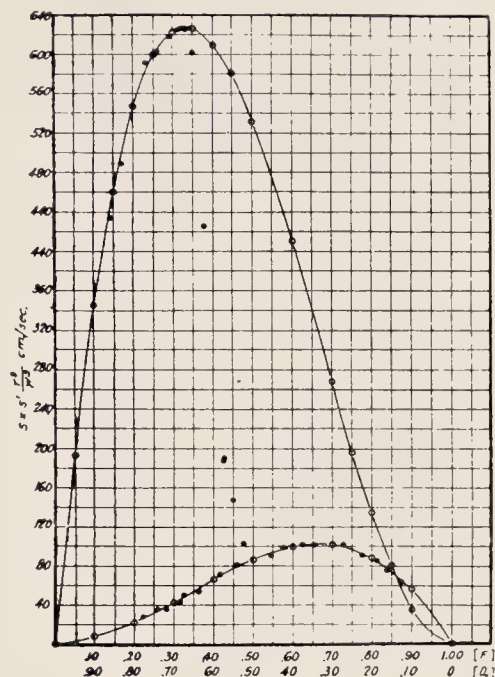
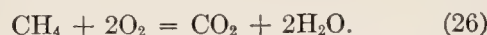
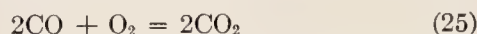


FIGURE 8

The proportion by volume with which the two gaseous components of F unite with oxygen may be taken as that given in their respective stoichiometric equations:



Then for pure carbon monoxide and oxygen,

$$s = k_1 [\text{CO}]^2 [\text{O}_2]. \quad (27)$$

The maximum value for s in this equation should be

$$s = k_1 [0.667]^2 [0.333], \quad (28)$$

CO O₂

which is confirmed by experimental results. And from the experimental results, the average value of k_1 was found to be

$$k_1 = s/[\text{CO}]^2 [\text{O}_2] = 691. \quad (29)$$

In Table I are set down the results obtained from the photographic records of this explosive reaction. The lower curve of Fig. 8 shows the plot of these results (solid dots). There is also shown the complete curve, represented by open circles and a continuous line, of the equation:

$$s = 691 [\text{CO}]^2 [\text{O}_2]. \quad (30)$$

For the methane-oxygen explosive reaction

$$s = k_1 [\text{CH}_4] [\text{O}_2]^2 \quad (31)$$

TABLE V

Rate of flame propagation in $\text{CH}_4 + 2\text{O}_2 \rightarrow$ explosive reaction

Record 11-21-27 No.	Partial pressure		$\Gamma = [\text{CH}_4][\text{O}_2]^2$	$s' = r_i/t$	$s = s'(r^3/r'^3)$	$k_1 = s/\Gamma$
	$[\text{CH}_4]$	$[\text{O}_2]$				
	atm	atm		cm/sec	cm/sec	
1 to 4	0.140	0.860	0.1035	3347	430	4155
5 to 8	0.170	0.830	0.1169	4536	488	4172
9 to 13	0.200	0.800	0.1280	5156	554	4326
14 to 17	0.230	0.770	0.1362	6048	596	4375
18 to 21	0.261	0.739	0.1425	6098	610	4280
22 to 25	0.291	0.709	0.1460	6359	615	4212
26 to 29	0.310	0.690	0.1476	6586	622	4212
30 to 33	0.320	0.680	0.1478	6636	621	4200
34 to 37	0.333	0.667	0.1478	6714	623	4213
						Av. 4240
38 to 41	0.346	0.654	0.1478	6586	598	4044
42 to 45	0.381	0.619	0.1457	4988	426	2903
46 to 49	0.425	0.575	0.1411	2808	188	1333
50 to 53	0.475	0.525	0.1308	1308	102	780

TABLE VI

Rate of flame propagation in a composite fuel, F, made up of a mixture of 95 parts by volume of carbon monoxide and 5 parts methane, with oxygen

Record 10-11-27 No.	Partial pressures		$\Gamma =$ $[\text{F}]^{1.91}[\text{O}_2]^{1.09}$	$s' = r_i/t$	$s = s'(r^3/r'^3)$	$k_1 = s/\Gamma$
	$[\text{F}]$	$[\text{O}_2]$				
	atm	atm		cm/sec	cm/sec	
1 to 4	0.226	0.774	0.0442	309	48.8	1007
5 to 8	0.275	0.725	0.0598	458	65.2	1090
9 to 12	0.325	0.675	0.0761	598	85.4	1123
13 to 16	0.375	0.625	0.0920	822	103.2	1123
17 to 20	0.416	0.584	0.1042	953	113.0	1084
21 to 24	0.474	0.526	0.1194	1150	130.0	1090
25 to 28	0.527	0.473	0.1300	1320	145.0	1117
29 to 32	0.578	0.422	0.1371	1357	154.0	1124
33 to 36	0.622	0.378	0.1397	1434	155.0	1108
37 to 40	0.676	0.324	0.1385	1426	154.0	1112
41 to 44	0.724	0.276	0.1326	1431	146.0	1101
45 to 48	0.776	0.224	0.1206	1296	136.0	1127
49 to 52	0.818	0.182	0.1064	1097	121.0	1137
						Av. 1103

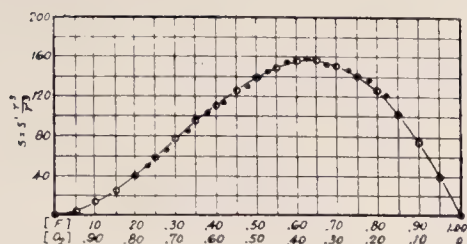


FIGURE 9

the maximum value for s should be

$$s = k_1 [0.333]_{\text{CH}_4} [0.667]_{\text{O}_2}^2. \quad (32)$$

This is found to agree well with observed results, and gives for the average value of k_1

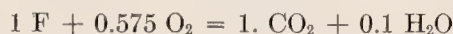
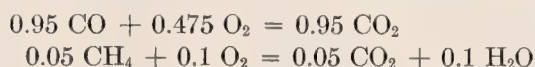
$$k_1 = s/[\text{CH}_4] [\text{O}_2]^2 = 4240. \quad (33)$$

The experimental results obtained from this reaction are given in Table V and plotted in the upper curve of Fig. 8 (solid dots). This figure also shows the complete curve, marked by open circles and a continuous line, of the equation

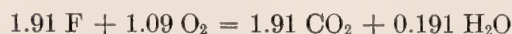
$$s = 4240 [\text{CH}_4] [\text{O}_2]^2. \quad (34)$$

For the case where the composition of the Fuel F is 0.95 part by volume of carbon monoxide and 0.05 part by volume of methane, the pro-

portion of oxygen necessary to satisfy the conventional formulas of its components for one part F would be



and for a trimolecular reaction,



$$s = k_1 [\text{F}]^{1.91} [\text{O}_2]^{1.09}. \quad (35)$$

The maximum value of s in this equation should occur for the composition

$$s = k_1 [0.637]_{\text{F}}^{1.91} [0.363]_{\text{O}_2}^{1.09}. \quad (36)$$

The average value of k_1 found is

$$k_1 = s/[\text{F}]^{1.91} [\text{O}_2]^{1.09} = 1103. \quad (37)$$

The experimental results obtained from the explosive reactions of this combination with O_2 are given in Table VI and plotted in Fig. 9, together with the complete curve for the equation

$$s = 1103 [\text{F}]^{1.91} [\text{O}_2]^{1.09}. \quad (38)$$

For the case where the composition of the Fuel F

TABLE VII

Rate of flame propagation in a composite fuel, F, made up of a mixture of 50 parts by volume of carbon monoxide and 50 parts methane, with oxygen

Record 11-1-27 No.	Partial pressure		$\Gamma =$ $[\text{F}]^{1.33} [\text{O}_2]^{1.67}$	$s' = r_i/t$	$s = s'(r^3/r'^3)$	$k_1 = s/\Gamma$
	[F]	[O ₂]				
	atm	atm		cm/sec	cm/sec	
1 to 4	0.175	0.825	0.0714	1579	223	3125
5 to 8	0.225	0.775	0.0898	2365	281	3128
9 to 12	0.275	0.725	0.1050	2879	325	3097
13 to 16	0.325	0.675	0.1163	3691	372	3198
17 to 21	0.375	0.625	0.1238	4148	395	3191
22 to 25	0.425	0.575	0.1272	4347	409	3215
26 to 29	0.473	0.527	0.1268	4073	400	3160
						Av. 3159
30 to 33	0.485	0.515	0.1262	3467	340	2697
34 to 37	0.498	0.502	0.1253	3568	336	2675
38 to 41	0.508	0.492	0.1243	3504	330	2659
42 to 45	0.521	0.479	0.1229	3455	311	2532
46 to 49	0.532	0.468	0.1215	3019	263	2164
50 to 53	0.555	0.445	0.1182	2530	219	1852
54 to 57	0.606	0.394	0.1084	1165	104	956

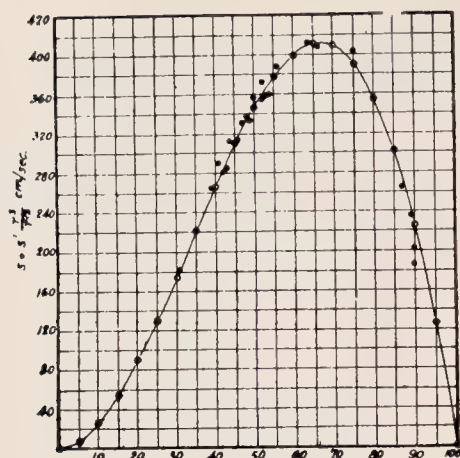
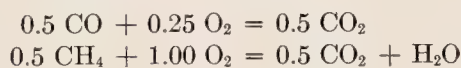
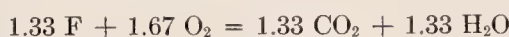


FIGURE 10

is 0.50 part by volume of carbon monoxide and 0.50 part by volume of methane, the proportion of oxygen necessary to satisfy the conventional formulas for one part F would be



and for a trimolecular reaction,



$$s = k_1 [\text{F}]^{1.33} [\text{O}_2]^{1.67}. \quad (39)$$

The average value of k_1 found is

$$k_1 = s/[\text{F}]^{1.33} [\text{O}_2]^{1.67} = 3159. \quad (40)$$

In Table VII are recorded the experimental results obtained from the fuel mixture, 0.50 part carbon monoxide and 0.50 part methane, with oxygen. These results (solid dots) are plotted in Fig. 10 together with the curve for the equation

$$s = 3159 [\text{F}]^{1.33} [\text{O}_2]^{1.67} \quad (41)$$

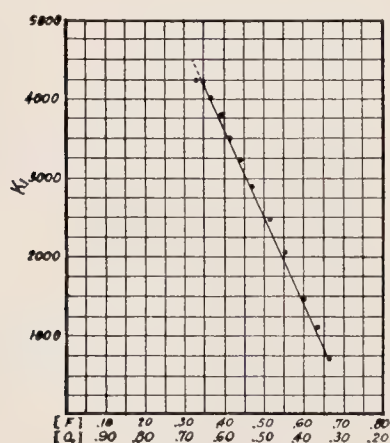


FIGURE 11

All the fuel combinations given in Table IV were investigated in the same manner as those described above. The results were tabulated and plotted.

In the coordinate Fig. 11 the ordinates represent values of the velocity constants of the reaction zone; the abscissas represent partial pressures of F and O₂. On this figure are plotted the values of k_1 against the corresponding partial pressures for maximum velocity of all of the fuel combinations of carbon monoxide and methane

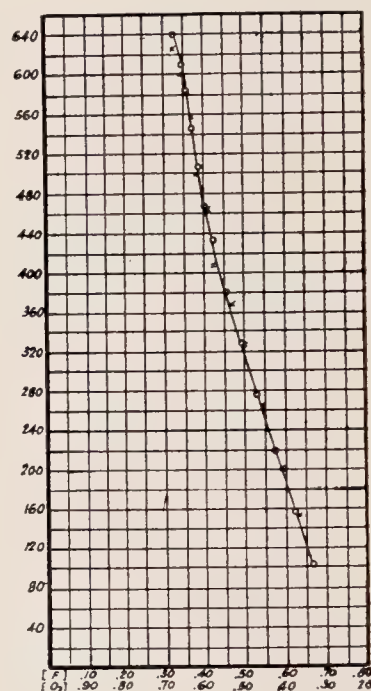


FIGURE 12

examined. It may be seen from this plot that these k_1 values follow closely a straight line drawn between the plotted values of k_{CH_4} and k_{CO} . This would indicate that the values of k_F are simple linear functions of the velocity coefficients of the reaction zone of its components k_{CH_4} and k_{CO} . The slope of this curve expressed in terms of the factors of the gaseous components is

$$C = \frac{k_{\text{CH}_4} - k_{\text{CO}}}{[n_{\text{CO}}/(n_{\text{CO}} + n_{\text{O}_2})] - [n_{\text{CH}_4}/(n_{\text{CH}_4} + n_{\text{O}_2})]}, \quad (42)$$

where the n 's represent the coefficients of the active gases in the respective stoichiometrical equations. Hence

$$C = \frac{4450 - 694}{0.667 - 0.333} = 11270. \quad (43)$$

The extension of this curve will cut the y -axis of the coordinate figure at 8206 and the x -axis at

0.728. The value of k_F for any composite fuel made up of any mixture of methane and carbon monoxide may then be written

$$k_F = 11270 \left(0.728 - \frac{n_F}{n_F = n_{O_2}} \right). \quad (44)$$

It is therefore possible from a knowledge of the velocity coefficients of the reaction zone of the methane and carbon monoxide explosive reactions to predict the flame velocity of any composite fuel, F , made up of methane and carbon monoxide; and that for any mixture ratio of F and oxygen that will ignite, since

$$s = k_F [F]^{n_1} [O_2]^{n_2}. \quad (45)$$

In the coordinate Fig. 12 the curve between the maximal values of $CH_4 + 2O_2 \rightarrow$ and $2CO + O_2 \rightarrow$ is the locus of the maximal values of s for all possible mixtures of methane and carbon monoxide with oxygen. This curve is calculated from Eq. (45). The points (X) near this curve are the observed maxima of the fuel mixtures given in Table IV.

Remarks

It will be seen by referring to Fig. 8 (upper curve) that the observed values of s for the $CH_4 + 2O_2 \rightarrow$ reaction no longer follow the curve for Eq. (34) after passing the point for its maximum value,

$$s = 4250 [0.333] [0.667]^2$$

CH₄ O₂

and that the deviation of the observed values of s from those given by Eq. (34) is, for those mixture ratios that will ignite, the greater the greater the excess of methane is over the theoretical amount of oxygen required to oxidize it. This abrupt decrease in the rate of propagation of the reaction zone—apparently related to the excess of methane

in the explosive mixture—may or may not be accompanied by a corresponding decrease in the amount of energy liberated. The constant-pressure method employed in these studies permits the determination of the actual work done by an explosive reaction. The constant-pressure bomb is an efficient experimental gas engine operating with minimum heat losses and negligible friction against the pressure of its surroundings. The photographic figures shown in Fig. 1 are engine diagrams to scale; r and r' represent the initial and final volumes of the reaction. The actual work accomplished by the transformation of a given charge is

$$W = c (r'^3 - r^3), \quad (46)$$

and for unit charge,

$$W/r^3 = c [(r'^3/r^3) - 1]. \quad (47)$$

In Fig. 13 the ordinates of the curve shown are values of $[(r'^3/r^3) - 1]$; the abscissas represent partial pressures of the active gases. The figure shows that, although the rate of reaction has been greatly reduced by an excess of methane, the total energy liberated has not been so affected. In fact, the maximum work appears to be obtained with a small excess of the fuel. The rapid decrease in the rate of the explosive reaction, however, due to an increase in the fuel excess, quickly prevents the possibility of maintaining a zone of explosive reaction in the mixture.

Acknowledgment

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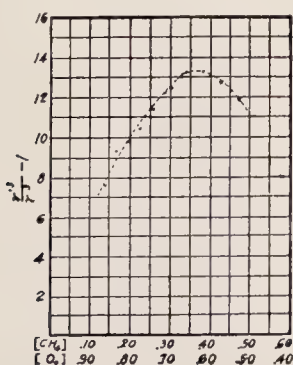


FIGURE 13

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THE "NORMAL" PROPAGATION OF FLAME IN GASEOUS MIXTURES

WILLIAM PAYMAN

Safety in Mines Research Board, Research Station, Harpur Hill, Buxton, Derbyshire, England

In this paper a preliminary attempt has been made to trace the relationships, where they exist, between the speeds of flame in mixtures of air with the constituents of the common industrial gases, hydrogen, carbon monoxide, methane (and other paraffin hydrocarbons), ethylene, and acetylene, inflamed under different conditions. It is hoped to extend these relationships as the result of work now in progress, and also to be able to examine systematically, and in somewhat greater detail, the exceptions to these relationships as they appear.

The study of gaseous combustion has proved so complex that the necessity of reducing the variable factors to a minimum in any one investigation has long been realized. Thus, notwithstanding the importance of the combustion of coal gas, for example, in industrial burners or in internal-combustion engines, experiments with coal gas under such practical conditions have not been largely favored by investigators in this field. The reasons for this are sound, and are based, firstly, on the fact that such industrial gases may vary considerably in composition, and results obtained with one particular gas may not hold with another gas, or even with another sample of the same type of gas from a different source. Secondly, the results obtained in a burner or engine of one particular design may apply only to the special conditions under which they have been obtained. In most of the systematic investigations which have been carried out on gaseous combustion, pure gases have been used and inflammation or explosion has been carried out under standard conditions usually much simpler than those obtaining in practice.

Though the utility of such a procedure is obvious, and considerable information of both a practical and theoretical nature has been obtained, the diversity of choice of apparatus, materials, and conditions which has been made by different investigators raises the question of whether some sort of connection cannot be found between the results thereby obtained, in order to be able to make the fullest use of them. It is essential to know not only how far the results obtained by one investigator can apply to and so supplement those obtained by another, but also how far the results obtained under such simplified conditions can be applied to the complex conditions of the practical utilization of inflammable gases in industrial operations.

The present paper describes a preliminary attempt to correlate some of the results obtained by diverse means. The record of simple relationships will serve to indicate the direct effect of change of particular factors, while exceptions to rules which apply to a large number of gases or

conditions will indicate the coming into play of other factors of importance whose study might be followed up with advantage.

The study of gaseous combustion is divided into four main and distinct branches—the ignition of gaseous mixtures, surface combustion, "normal" inflammation,¹ and detonation. Though there can be no doubt that these branches are interconnected in many ways, it would be extremely difficult to trace any connection at the present stage of our knowledge. Only the third branch, that concerned with the "normal" propagation of flame, will be discussed here, and consideration will be limited to the inflammable constituents of the common industrial gases—namely, hydrogen, carbon monoxide, methane (and other paraffin hydrocarbons), ethylene, and acetylene—in admixture with air.

Inflammation of Different Gas Mixtures Under Constant Conditions

If the rate of flame propagation is measured in a series of mixtures of any one inflammable gas with air under any one constant set of conditions, the variation in rate with concentration always follows the same sequence. Below a certain concentration of inflammable gas, known as the "lower limit of inflammability," continuous self-propagation of flame does not take place. As the percentage of inflammable gas is increased the speed of propagation of flame in the mixture increases above the speed in the limit mixture. This increase always continues until the concentration of inflammable gas is higher than that in the mixture for complete combustion, by an amount which has been termed the "displacement" of the "maximum-speed mixture." Further addition of inflammable gas causes a decrease in the speed of flame until the "upper limit of inflammability" is reached, and mixtures containing a higher concentration of inflammable gas than this are again incapable of supporting the continued propagation of flame.

A number of speed-percentage curves showing the manner of this variation with the gases

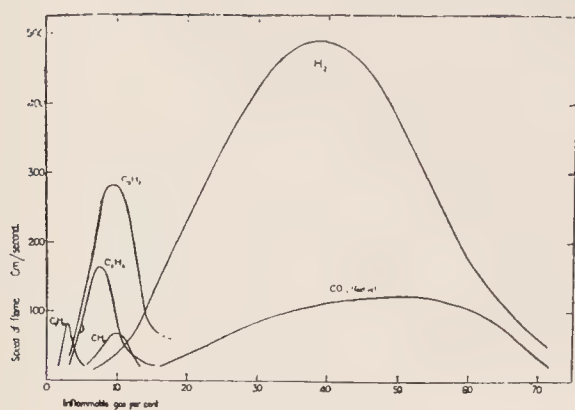


Diagram 1

considered in this paper—hydrogen,² carbon monoxide,³ methane,⁴ pentane,⁴ ethylene,⁵ and acetylene⁶—are given in Diagram 1. The speeds are those of the “uniform movement” of flame in a horizontal tube 2.5 cm in diameter. The uniform movement⁷ is the initial stage in the propagation of flame when a gas mixture is ignited at the open end of a cylindrical tube closed at the other end. These curves indicate the wide difference in the ranges of inflammable air mixtures and also in the maximum uniform movement of flame with different inflammable gases. The use of the term “effective” in connection with the speeds of flame with carbon monoxide is explained later.

There are two main features of similarity shown by gases: (1) the “displacement” of the “maximum-speed mixture” from that which contains inflammable gas and oxygen in combining proportions, to which reference has already been made; and (2) the speed of flame in the limit mixtures which, with a few exceptions, is approximately 20 cm. per second.

Displacement of Maximum-Speed Mixture. Various explanations have been advanced for the displacement of the maximum-speed mixtures. When first observed with hydrogen–air mixtures,⁸ it was suggested that it was due to the thermal conductivity of hydrogen being greater than that of air, but later a similar displacement was found with other inflammable gases whose thermal conductivity was equal to or less than that of air. The mixtures of carbon monoxide and air and of hydrogen and air which give the maximum explosion pressures also contain excess of inflammable gas, and this displacement has been shown to be due to dissociation.⁹ The displacement of the maximum-speed mixture cannot be due to the same cause, because, firstly, the displacement is found with gas mixtures (mixtures of inflammable gases with a “reduced-oxygen atmosphere”) in which the temperature is too

low for dissociation to be appreciable and, secondly, the displacement is sometimes much larger with the maximum-speed mixture than with the maximum-pressure mixture—for example, with hydrogen–air mixtures (10 per cent for maximum-speed mixture² and 3 per cent for maximum-pressure mixture¹⁰). Further it has been shown that in mixtures of methane with what have been termed argon or helium “atmospheres,” that is, with air in which the nitrogen has been replaced by argon or helium—the displacement is the same as with methane–air mixtures, although the temperatures attained must be much higher and therefore the amount of dissociation must be much greater.¹¹

An alternative suggestion has been advanced¹² which assumes that the speed of flame is dependent upon the rate of reaction between the inflammable gas and the oxygen in the gas mixture, and therefore upon the temperature and concentration of the reacting gases. Whereas the maximum-temperature mixture, assuming no dissociation, is that for complete combustion, it can be deduced from the law of mass action that active masses of reacting gases are greatest when excess of inflammable gas is present, when that gas is mixed with a constant-proportion nitrogen–oxygen mixture such as air, so that the maximum-speed mixture is always displaced in that direction. It may be further deduced that if oxygen were mixed with a constant-proportion mixture of nitrogen with an inflammable gas the displacement would be toward mixtures containing excess of oxygen. The most important conclusion for practical purposes is that the displacement will not occur¹ when the inflammable gas contains an appreciable quantity of inert gas, such as a producer gas, when mixed and inflamed with air;

TABLE I

Speed of uniform movement of flame in limit mixtures of various inflammable gases in air

Inflammable gas	Lower limit mixture	Upper limit mixture
	cm/sec	cm/sec
Carbon monoxide ³	19.5	19.4
Methane ⁴	23.3	19.1
Ethane ⁴	18.1	19.7
Propane ⁴	20.8	20.3
Butane ⁴	20.1	20.3
Pentane ⁴	20.2	20.2
Ethylene ⁵	23.1	22.0

and (2) when an inflammable gas or gas mixture containing no noninflammable constituents is mixed and inflamed with pure oxygen.^{3,12}

The Speed of Uniform Movement of Flame in Limit Mixtures. Despite the wide variation in the maximum speed of uniform movement of flame attainable in air mixtures of different inflammable gases, the speeds in the limit mixtures of the gases we are considering tend toward a constant value, about 20 cm per second in a horizontal glass tube 2.5 cm in diameter, as the values in Table I indicate.

A similar agreement is found with limit mixtures of methane with different "atmospheres" of oxygen and nitrogen.¹³ A satisfactory explanation of this agreement has not yet been advanced. Notable exceptions to it are acetylene and hydrogen. Acetylene is endothermic and at the upper limit decomposes depositing carbon. Hydrogen is peculiar in that at the lower limit tiny balls of flame are formed and seem capable of being propagated indefinitely.

Propagation of Flame in a Closed Cylinder

The uniform movement is perhaps the simplest phase of propagation, and comparison can readily be made between the constant speeds obtained in each mixture. Where the propagation is not uniform, however, it is not easy to compare speeds, which may be changing continuously. Mean speeds have therefore to be used, so that in practice the times are measured for the flame to travel over the same portion of the same vessel. Thus in a closed cylinder the rates of propagation are most conveniently compared by measuring the time intervals between the instant of passage of the igniting spark and the moment at which the flame reaches the end or ends of the vessel, in the same way as the rates of rise of pressure in a closed vessel may be compared by measuring the time taken for attainment of maximum pressure after the passage of the spark.

Since the movement of the flame in a closed vessel is usually not uniform, and the speed of any one flame may vary within quite wide limits, it might be doubted whether any real comparison could be made between the rate of propagation of flame in different gas mixtures when exploded under such conditions.

A series of experiments is being carried out¹⁴ in which careful photographic (moving-film) records are being made of the passage of flame from the center to the ends of a closed brass cylinder, 20 cm long and 5 cm in diameter, the photograph being taken through a long, narrow window in one side of the explosion vessel. Though

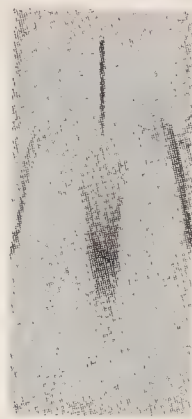


FIGURE 1

these experiments are not yet complete, some very interesting results have already been obtained, which indicate that the manner of flame propagation in such a vessel remains the same with a large variety of gaseous mixtures, provided, of course, that the strength and position of the source of ignition, an electric spark, are unaltered.

A typical photograph is reproduced in Fig. 1, an explanatory diagram being given in Fig. 2. In the diagrams at the bottom of Fig. 2, the position of the slit in the brass vessel is indicated, and the direction of movement of the flame is shown by the arrows. The film moved upward. The mixture was of acetylene and air containing 6.5 per cent of inflammable gas, and the initial pressure was a quarter of an atmosphere. It will be seen that the flame appears the moment the spark passes, and spreads out symmetrically toward each end of the explosion vessel. It accelerates from the point of ignition, but about two-thirds of the way along the tube slows down rather suddenly and passes more slowly to the ends of the tube.

In the present paper we are concerned mainly

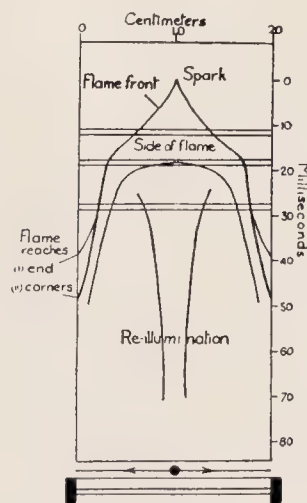


FIGURE 2

with the rate of propagation of the flame, and so the portion of this and similar photographs to be considered is the flame front only. The main feature of such photographs is the arrest of the flame. A flame arrest has frequently been noted by investigators examining the movements of flame in gaseous mixtures contained in closed vessels, and different explanations have been offered to account for it. One¹⁵ is that the arrest is due to the compression wave from ignition, moving at the speed of sound in the unburnt gases and being reflected from the far end of the tube. The second explanation¹⁶ involves assumptions of gas surging or gaseous movements *en masse*, it being held, in general, that the arrest marks a point at which pressure behind the flame becomes equal to the pressure in front.

The following alternative explanation has been recently advanced¹: When an inflammable gas mixture is ignited at a point within a closed vessel, flame spreads simultaneously in all directions. During the first stage of propagation, before the flame touches the walls of the containing vessel, little heat will be lost by the flame, save to unburnt gases, except that lost by radiation. When the flame touches the walls of the tube a second phase commences, heat being lost to the walls by conduction as the flame travels along in contact with them, both by the flame and the hot gases behind the flame, and the flame speed is reduced. In a cylinder the flame commences to spread spherically, but soon becomes egg-shaped, as is shown in the series of flame snapshots in Fig. 3¹⁸ (taken with a different gas mixture and in a similar vessel but of different dimensions), so that the most forward portion of the flame in each direction has traveled some distance along the tube before its equatorial belt has touched the walls. The distance between the two ends of the flame may be quite large

compared with the diameter of the tube before the portion touching the walls first is extinguished by them at that point. This extinction at the sides of the egg-shaped flame will result in propagation being now carried on solely by the two ends—that is, by two separate flames moving in opposite directions. Retardation probably commences as soon as the flame touches the walls or comes close enough to lose an appreciable amount of heat to them. The definite arrest of the flame would correspond to the moment of separation of the flame into two portions, so that the arrest would necessarily be simultaneous on each side of the point of ignition. The simultaneous arrest of the flame front takes place not only under the conditions of the present experiment, but also under conditions such that the flame moves at appreciably different speeds toward the two ends of the tube.¹⁹

The sequence of affairs is shown in Figs. 1 and 2. The flame may be regarded, before it breaks, as a luminous shell (like an eggshell) enclosing a nonluminous space. The outer edges of the flame—that is, the portions advancing toward the ends of the tube—are in line with the axis of the camera, which, therefore, records a considerable depth of flame and shows up as a dark black line whose width gives some indication of the (maximum probable) thickness of the flame front. The portions near the side of the tube are at right angles to the camera axis, and the depth of flame recorded is much less, so that the sides of the flame do not appear so black. At any one instant the position of the flame behind the slit in the explosion vessel is indicated by a narrow horizontal section of the photograph. Three such sections are shown in Fig. 2. At the instant shown in the uppermost section the flame is a complete spherical or egg-shaped shell. From the moment of ignition to the instant corresponding to the

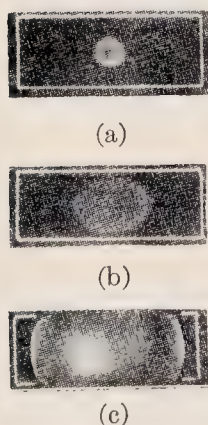


FIGURE 3

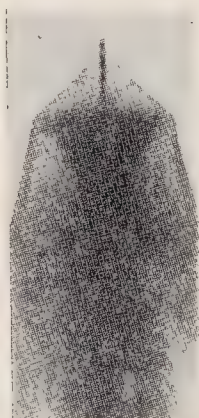


FIGURE 4



FIGURE 5



FIGURE 6



FIGURE 7

middle section the flame front has been accelerating, and the shell has been unbroken. Now, however, the flame is breaking and the break is rapidly increasing in size. At approximately the same instant the flame front begins to slow down. At the instant shown in the third section two distinct flames are observed, traveling in opposite directions. (Compare Fig. 3.)

Having considered the mode of propagation of flame in one particular mixture in this vessel, we may proceed to examine the effect of change of conditions—initial pressure, for example—and of change of composition of the mixture, or of the type of inflammable gas. Figure 4 shows the result of a repeat experiment similar to that for Fig. 1, except that the initial pressure was atmospheric instead of only one quarter of an atmosphere. The record of the flame front is identical in Figs. 1 and 4, although the after-effects, the re-illumination noted in all the records, are far less pronounced at the lower pressure, indicating that *they* have no effect on the speed of the flame.

To proceed next to the effect of change of inflammable gas, we may note the effect of addition of hydrogen to the acetylene. Figure 5 shows the mode of spread of flame in an air mixture with an inflammable gas of the composition $C_2H_2 + H_2$, the particular mixture being chosen because the speed of flame is approximately the same in it as in the mixture of acetylene along with air shown in Fig. 1. The records of the flame front are almost identical. A record of a far different mixture, which shows a greatly increased re-illumination after the flame has passed but approximately the same flame-front record, is shown in Fig. 6, the mixture in this instance being $2CO + O_2$, at an initial pressure of half an atmosphere and saturated with water vapor at $15^\circ C$.

A complete series of determinations has been made with mixtures of ethylene and air in the same vessel and the point of arrest noted. It was found to be the same with all mixtures, whatever the speed, except at the limits of inflammability, where convection currents apparently come into play. The same point of arrest was also noted when mixtures of methane, ethane, propane, pentane, and acetylene were inflamed with just sufficient air to allow of their complete combustion to carbon dioxide and steam.

Comparison of Speed-Percentage Curves Obtained Under Different Conditions

It is therefore possible to obtain conditions which should be comparable, even when the spread of flame is not uniform, and to examine how far comparisons made under one set of

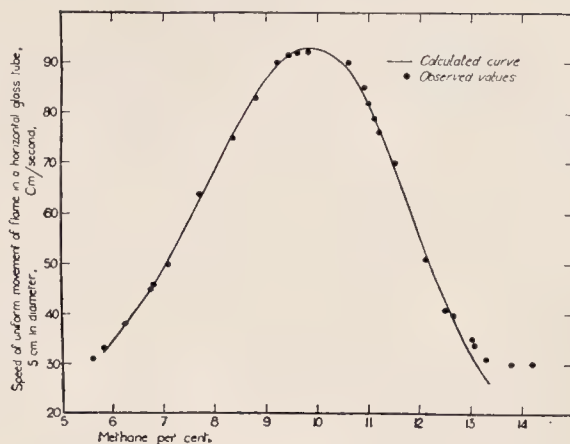


Diagram 2

conditions agree with those made under different conditions. This will now be discussed with the assistance of a series of speed-percentage curves.

Uniform Movement of Flame in Tubes of Different Diameter. The most accurate and complete determinations of the speed of uniform movement of flame are those for mixtures of methane and air determined in horizontal tubes of 2.5- and 5-cm diameter. The maximum speeds of flame in methane-air mixtures in these tubes are 66.6^4 and 93.0^7 cm per second, respectively. From the values obtained in the 2.5-cm tube a smooth curve was constructed by multiplying throughout by a factor 1.4 ($93.0:66.6$). This smooth curve is shown in Diagram 2, while the dots show the values actually obtained in a 5-cm tube for the whole series of mixtures.²⁰ It will be seen that, except close to the upper limit, the observed values lie on the calculated curve. The relationship here is therefore very close. A similar relationship is observed with the other hydrocarbons, as shown in Table II, in which are given the observed values in the 5-cm tube and the values calculated from those obtained in the 2.5-cm tube, for the maximum-speed mixtures in air, by multiplication by the same factor (1.4).

Acetylene is the only other gas whose mixtures

TABLE II

Speed of flame in tubes of different diameter

Diameter of tube	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
cm	cm/sec	cm/sec	cm/sec	cm/sec
2.5 Obs. ⁴	85.6	82.1	82.6	83.0
5.0 Obs. ²⁰	120	115	115	116
5.0 Calc.	127	114	113	115

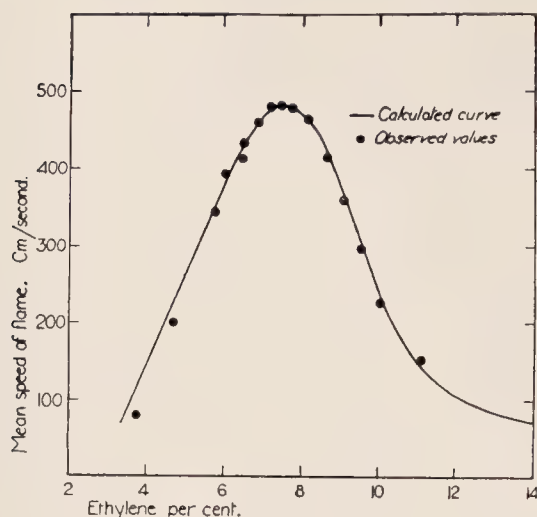


Diagram 3

with air have been examined and the speed of uniform movement of flame determined in its mixtures with air in tubes of these dimensions. The calculated value for the uniform movement of flame in a 5-cm tube using the same factor is 395, but the value found is only 312 cm per second. As acetylene has also been found to be an exception to other relationships, the reason for its non-agreement should prove of interest. It is probably due to the endothermic nature of this gas. But it may also be noted that in an acetylene-air explosion the acetylene may combine not only with the oxygen but also with the nitrogen of the air.^{21,22} Both these factors may be influenced by the pressure effect of confinement.

Uniform Movement of Flame and Propagation of Flame in a Closed Cylinder. The maximum speed of uniform movement of flame in ethylene-air mixtures in a horizontal glass tube, 2.5 cm in diameter, is 166 cm per second.⁵ The maximum

TABLE III

Time for reaching maximum pressure

Inflammable gas	Reference	Found	Calculated
		sec	sec
CH ₄	27	0.067	0.067
C ₂ H ₆	27	0.050	0.052
C ₃ H ₈	27	0.055	0.054
C ₄ H ₁₀	27	0.054	0.054
C ₅ H ₁₂	27	0.056	0.054
C ₂ H ₄	28	0.027	0.027
H ₂	29	0.007	0.009

mean speed of propagation of flame in such mixtures from the center to the ends of the brass cylinder in which the photographic records in Fig. 1, etc., were taken is 482 cm per second.²³ From the values obtained for the uniform movement of flame a smooth speed-percentage curve has been obtained by multiplying throughout by a factor 2.9 (482:166). This curve is shown in Diagram 3, on which the black dots show the speeds obtained in the closed cylinder for the whole series of air mixtures.⁵ The agreement is remarkably good over the whole of the determined range.

Uniform Movement of Flame and Rate of Rise of Pressure in a Closed Sphere. It has been shown²⁴ that when a gas mixture is ignited centrally in a closed sphere the time taken for attainment of maximum pressure is the same as for the flame to reach the walls of the containing vessel, both being measured from the moment of ignition,

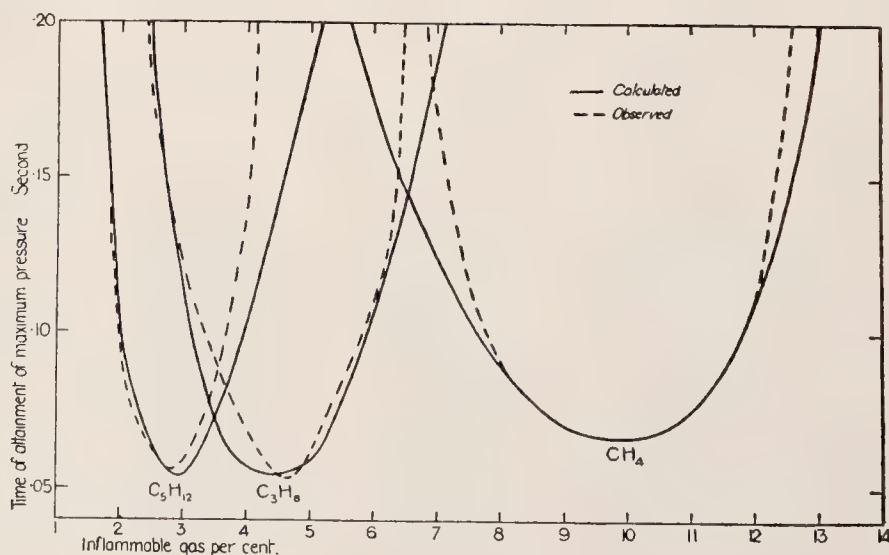


Diagram 4

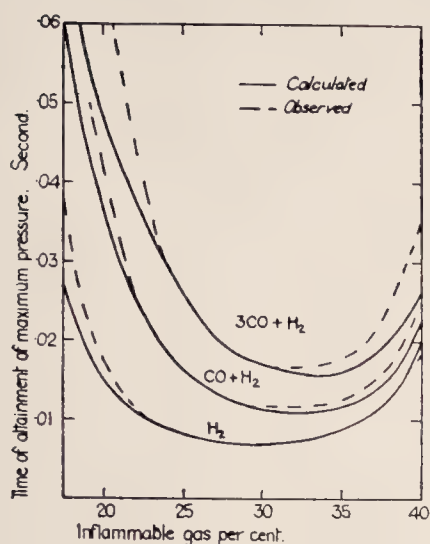


Diagram 5

except with slowly moving flames near the limits of inflammability.

The time of attainment of maximum pressure in the maximum-speed mixture of methane-air when ignited centrally in a 4-liter sphere is 0.067 second.¹⁴ The maximum speed of the uniform movement of flame in a horizontal glass tube 2.5 cm in diameter is 66.7 cm per second, from which a constant $0.067 \times 66.7 = 4.47$ is obtained, and assuming time (4-liter vessel) \times speed (uniform movement) is constant, the times of attainment of maximum pressure in other mixtures may be calculated. The results of such calculations are given in Table III, and are compared with the observed values.

The agreement is shown to be quite good for maximum-speed mixtures. In order to find whether the agreement is as good for the full range of air mixtures of each gas, two sets of "smooth calculated curves" have been drawn as before. The first set (Diagram 4) shows calculated and observed values for the gases methane, propane, and pentane, the second (Diagram 5) for H_2 , $CO + H_2$, and $3CO + H_2$. The two sets are not shown on the same scale, since the order

of time is so vastly different. For the same reason a factor has been chosen for Diagram 5 calculated from the hydrogen results—namely, $485 \times 0.007 = 3.4$. The agreement is, in general, quite good, but it will be seen that the curves for propagation of flame in the sphere are steeper than the uniform movement curves, an important difference and possibly an effect of the difference in confinement.

Uniform Movement of Flame and Height of Bunsen Cone with Different Inflammable Gases. It is known that the height of the Bunsen cone with a given gas mixture, and the tendency of the flame in that mixture to fire-back in the burner, depend upon the speed of propagation of flame in it. The height of the Bunsen cone has indeed been used as a means of measuring the speed of propagation of flame.^{28,29,30} In one series of determinations by this method a speed of 27.2 cm per second was obtained as the maximum for methane-air mixtures. The method has also been used for hydrogen-air, acetylene-air, and ethylene-air mixtures, and the results³⁰ are shown in Diagram 6, where they are compared with corresponding curves calculated from the speeds of uniform movement of flame in a 2.5-cm tube by multiplying throughout by a factor obtained from the maximum speeds of flame obtained by the two methods with methane-air mixtures. This factor is 0.408 (27.2:66.6). The Bunsen method gives results for the speed of flame which are somewhat erratic, and the rough correspondence of the curves in this diagram may be considered satisfactory. The relative speeds are of the same order, though the observed speed for ethylene is rather high. With an inflammable gas mixture of the composition $CO + H_2$ the maximum speed was found to be 137 cm per second. The value calculated for this mixture is 131 cm per second.

The calculated and observed maximum speeds for hydrogen are approximately the same, but the curves are appreciably displaced. It has been shown, however, that the important feature of the speed-percentage curves from the point of view of utilization of gaseous fuels in industrial burners³¹ is the slope of the curves on the upper-limit side, and the two curves agree quite well in this respect. The significance of these measurements is that the height of the Bunsen cone is inversely proportional to the speed of propagation of flame with a given mixture.

Effect of Size of Vessel. The effect of size of vessel on the speed of flame has only been examined, with an appreciable range of sizes, with the uniform movement of flame, and in methane-air mixtures.³² Diagram 7 shows the similarity of the curves obtained with tubes of different diameter.

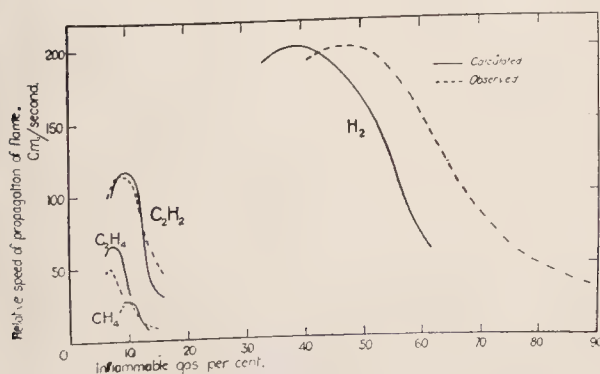


Diagram 6

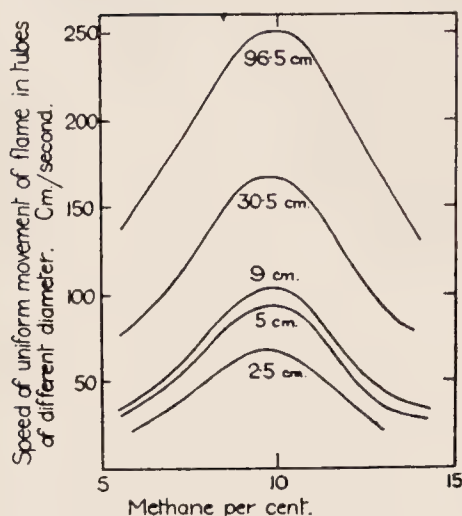


Diagram 7

Experiments with closed vessels have been mainly limited to low capacities, and little information is available as to the effect of considerable increase in size of explosion vessel. It has been shown that when methane-air mixtures are ignited centrally in a closed sphere the mean speed of the flame is the same when the capacity is 4, 16, or 32 liters.²⁴

A photographic investigation of the spread of flame in large cylinders is being carried out at present,³³ and two of the photographs obtained with methane-air mixtures, in a cylinder 50 cm long and 10 cm in diameter, are shown in Figs. 7 and 8. Figure 7, in which ignition was central, may be compared with the earlier photographs in this paper, obtained by using an explosion cylinder only 20 cm long and 5 cm in diameter. Figure 8 shows the movement of flame in the large vessel when ignition is at one end. Figure 9

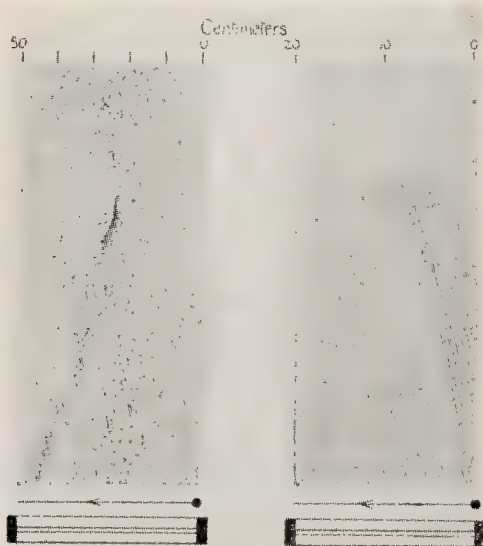


FIGURE 8

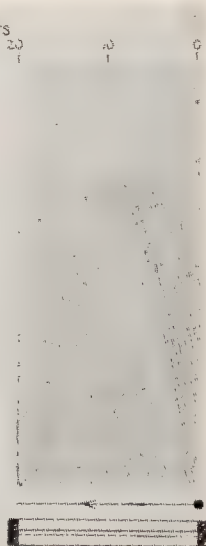


FIGURE 9

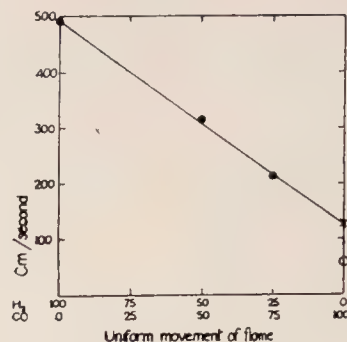


Diagram 8

shows a similar photograph of the spread of flame in the small cylinder with ignition at one end.²³ The similarity is marked. A speed-percentage curve is not available for the larger vessel. When the length of the vessel is increased still further, vibrations are set up and the character of the flame propagation is then altered.

Combustion of Carbon Monoxide

Carbon monoxide is an important constituent of many industrial fuel gases, but attempts to compare the speeds of flame in carbon monoxide-air mixtures under different conditions are hindered by the fact that the speed of propagation of flame in a given mixture of carbon monoxide with air is dependent on the degree of saturation with water vapor,³ the speed increasing to a maximum when about 6 per cent of water vapor by volume is present. This maximum value has been termed the "effective speed" of carbon monoxide,³ and is the value carbon monoxide may be presumed to have when fuel gases are used. All such gases contain hydrogen, a small quantity of which gives to carbon monoxide its maximum speed of flame. This point is illustrated by Diagrams 8 and 9 in which are plotted the speeds of flame during (1) the uniform movement³ and (2) flame propagation in a sphere with central ignition,²⁷ for two series of maximum-speed carbon monoxide-hydrogen mixtures. The

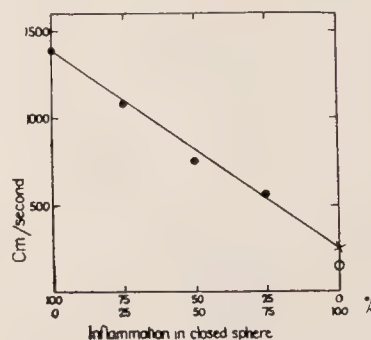


Diagram 9

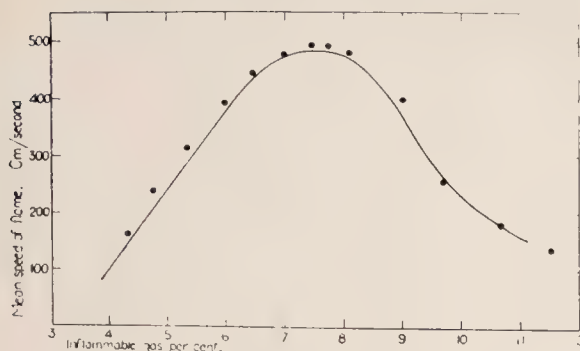


Diagram 10

effective speed of carbon monoxide (with about 6 per cent of moisture) is shown in each diagram by a cross, and the observed value with only 2 per cent moisture (saturated at 15°C) is shown by an open circle.

Determination of Absolute Values of Speed of Flame

The deduction of the absolute value of the speed of flame is obviously a matter of considerable difficulty. The speed of flame in a mixture of air with one concentration of inflammable gas cannot as yet be calculated from that with another concentration of the same gas, nor can the factors used in the calculations earlier in this paper be deduced, but the correlation of the values carried out here may possibly be suggestive and of assistance in formulating a method of so doing.

A still more difficult task would be the determination of the relationship between the maximum-speed, say, of one inflammable gas and that

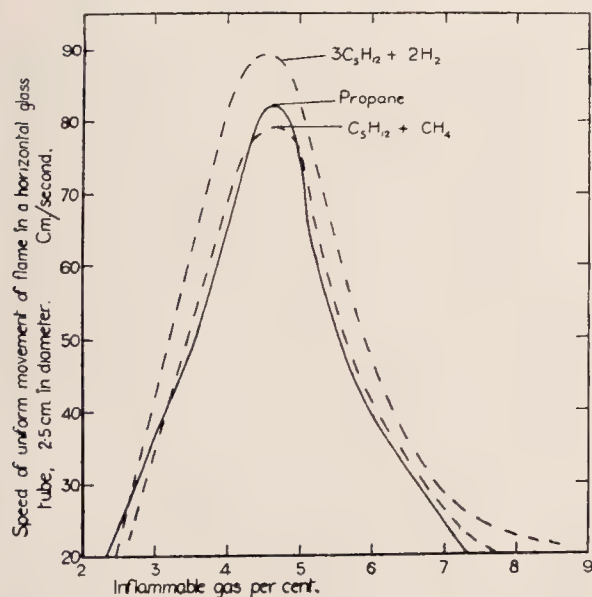


Diagram 11

of another. It is not easy, for example, to explain the great difference in the maximum speed of flame in hydrogen-air and carbon monoxide-air mixtures, both inflammable gases having the same oxygen requirements for complete combustion and the same calorific value.

With the hydrocarbon gases the relationship is possibly simpler. One method of tracing this relationship is to compare the speeds of flame in air mixtures of a given inflammable gas and a mixture of two other inflammable gases equivalent to the first in density and carbon-hydrogen ratio. Thus the mixture $C_2H_6 + C_2H_2$ is equivalent to ethylene (C_2H_4) and either $C_5H_{12} + CH_4$ or $3 C_5H_{12} + 2 H_2$ is equivalent to propane (C_3H_8). It must be noted that $C_2H_2 + H_2$ is not

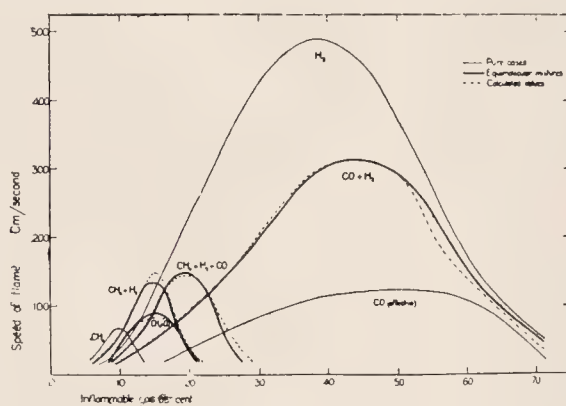


Diagram 12

equivalent to ethylene, because though the carbon-hydrogen ratio of this gas is the same its density is only half that of ethylene.

In Diagram 10 the continuous curve shows the speeds of propagation of flame from observed values in the closed cylinder 20 cm long with ethylene-air mixtures,²³ while the dots show experimentally determined values for the equivalent mixture $C_2H_2 + C_2H_6$. There is a close correspondence.

In Diagram 11 the continuous curve shows the speeds of uniform movement of flame in a tube 2.5 cm in diameter for propane-air,¹³ while the dotted curves show the speeds in the equivalent mixtures $C_5H_{12} + CH_4$ and $3 C_5H_{12} + 2 H_2$. Through the agreement with the mixture containing hydrogen is not so good as with the hydrocarbon mixture, it still seems close when the great differences in the maximum speeds and the ranges of inflammability, of the constituent gases, pentane and hydrogen, are compared (see Diagram 1).

Law of Flame Speeds

These few results are instructive, and should prove of value as an aid to the law of flame speeds

in further investigations. The law of flame speeds is a simple additive relationship for calculating the speed-percentage curves for complex inflammable gases from the curves with the simple constituent gases. This relationship has been developed in detail in a number of papers^{3,4,11,12,27,34-37} and will not be discussed here, but a comparison of calculated and observed speed percentages will be of interest from the point of view of the present paper, and such a comparison is made in Diagram 12 for equimolecular mixtures of methane, hydrogen, and carbon monoxide, and will indicate the utility of the speed law.

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GASEOUS EXPLOSIONS. VI. FLAME AND PRESSURE PROPAGATION*

J. V. HUNN AND GEORGE GRANGER BROWN

University of Michigan, Ann Arbor, Michigan

This investigation was undertaken in order to obtain experimental data concerning the relation between flame propagation and the pressure changes resulting therefrom. The apparatus used and its method of operation are described in detail and the experimental data are interpreted and discussed.

Although many investigators have photographed the movement of the flame in gaseous explosions, and some have recorded the rise in pressure at one point in the explosion chamber while photographing the flame, practically all conclusions concerning the pressure effect accompanying the flame are entirely speculative, as no experimental data have been reported giving the pressures developed by and accompanying the flame as it progresses through the explosive mixture.

Many investigators have observed a halt in the advance of the flame front as it progresses through the explosive mixture. The cause of this halt has been explained in various manners. Dixon¹ believes it to be due to a reflected pressure wave set up by the igniting spark and traveling through the unburned gases ahead of the flame. After being reflected from the far end of the explosion chamber it meets the flame front before the flame front reaches the end of the explosion chamber.

Woodbury, Lewis, and Canby² observed this halt in the flame front when photographing the flame and recording the pressures developed at the end of the explosion chamber opposite the point of ignition, and explained it in the following manner:

It has been previously shown that the flame front is pushed forward by the expansion of the burned gases and that the unburned gases are compressed to a high density at the same time. Obviously a point can be reached at which the pressure due to the temperature behind the flame is equaled by the pressure due to the density ahead of the flame. At that point the flame front is no longer pushed forward; the propagation is arrested.

Midgley³ and Janeway developed mathematical treatment of progressive flame travel up to the detonation wave based on the assumption that the pressure ahead of the flame must be greater than the pressure behind the flame in order to

supply the energy required to push the unburned gas into the flame and give the particles behind the flame their velocity to the rear of the flame front. They furnish no experimental evidence to support this assumption.

Apparatus

The apparatus may be divided into four major parts: (1) the bomb and assembly, (2) the pressure recorder, (3) the flame recorder, and (4) the wiring and timing mechanism.

Bomb and Assembly. The bomb was made from a special steel casting, 114.3 cm (45 inches) long and 15.2 cm (6 inches) square with a 7.62-cm (3-inch) diameter cylindrical hole cast lengthwise through the center. The casting was cut off 12.7 cm (5 inches) from each end to insure sound metal. This left 88.8 cm (35 inches) over-all as the length of the bomb casting.

A circular tongue, 7.62 cm (3 inches) i.d. and 10.1 cm (4 inches) o.d. at the base and 8.9 cm (3.5 inches) o.d. at the top, was turned on each end of the bomb as shown in Fig. 3. The ends of the bomb were closed with a cast-iron plate 15.2 cm (6 inches) square and 3.8 cm (1.5 inches) thick grooved to fit the tongue on the ends of the bomb and held in place by four heavy cap screws. A rubber gasket was placed in the bottom of the groove in the cast-iron plate to make the joint gas-tight.

A slot 1.27 cm (0.5 inch) wide was cut lengthwise through the bomb on one side to act as a window for photographing the flame. Three bridges 1.27 cm (0.5 inch) wide and a bridge at each end 2.54 cm (1 inch) wide were left across the slot for strengthening and gasket supports. This slot was covered with two plate-glass windows 5.1 cm (2 inches) wide, 0.63 cm (0.25 inch) thick, and 43.2 cm (17 inches) long set into a recess cut in the bomb over the slot. A rubber gasket was placed between the glass and the metal of the bomb. Two bars of steel 86.3 cm (34 inches) long, 1.9 cm (0.75 inch) wide, and 1.27 cm (0.5 inch) thick were placed on top of the glass, but separated from it by a rubber gasket, along each side of the window recess.

* Part of a thesis submitted by J. V. Hunn in partial fulfillment of the requirements for the degree of doctor of philosophy in the University of Michigan.

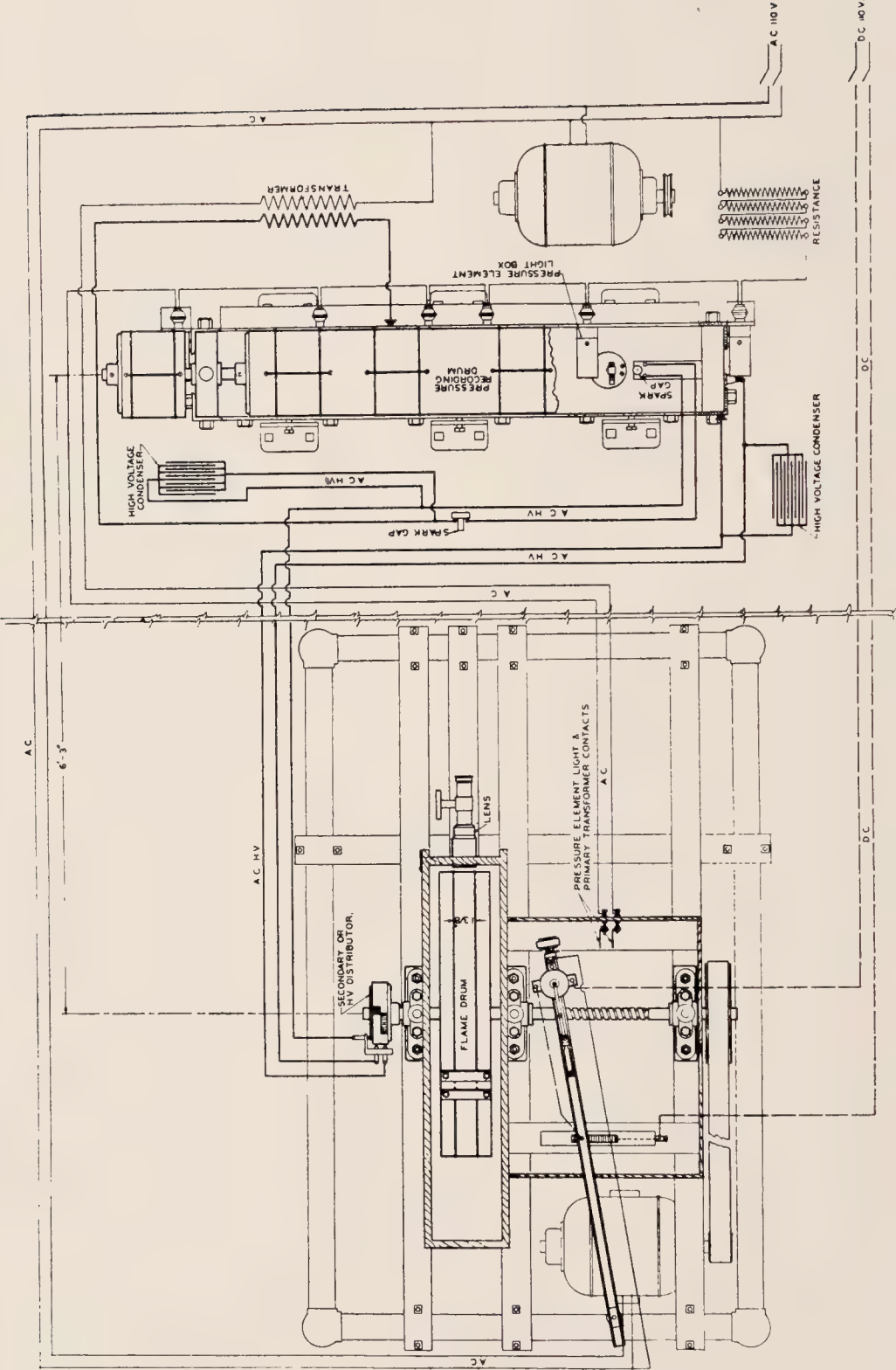


Fig. 1. Assembly and wiring diagram.

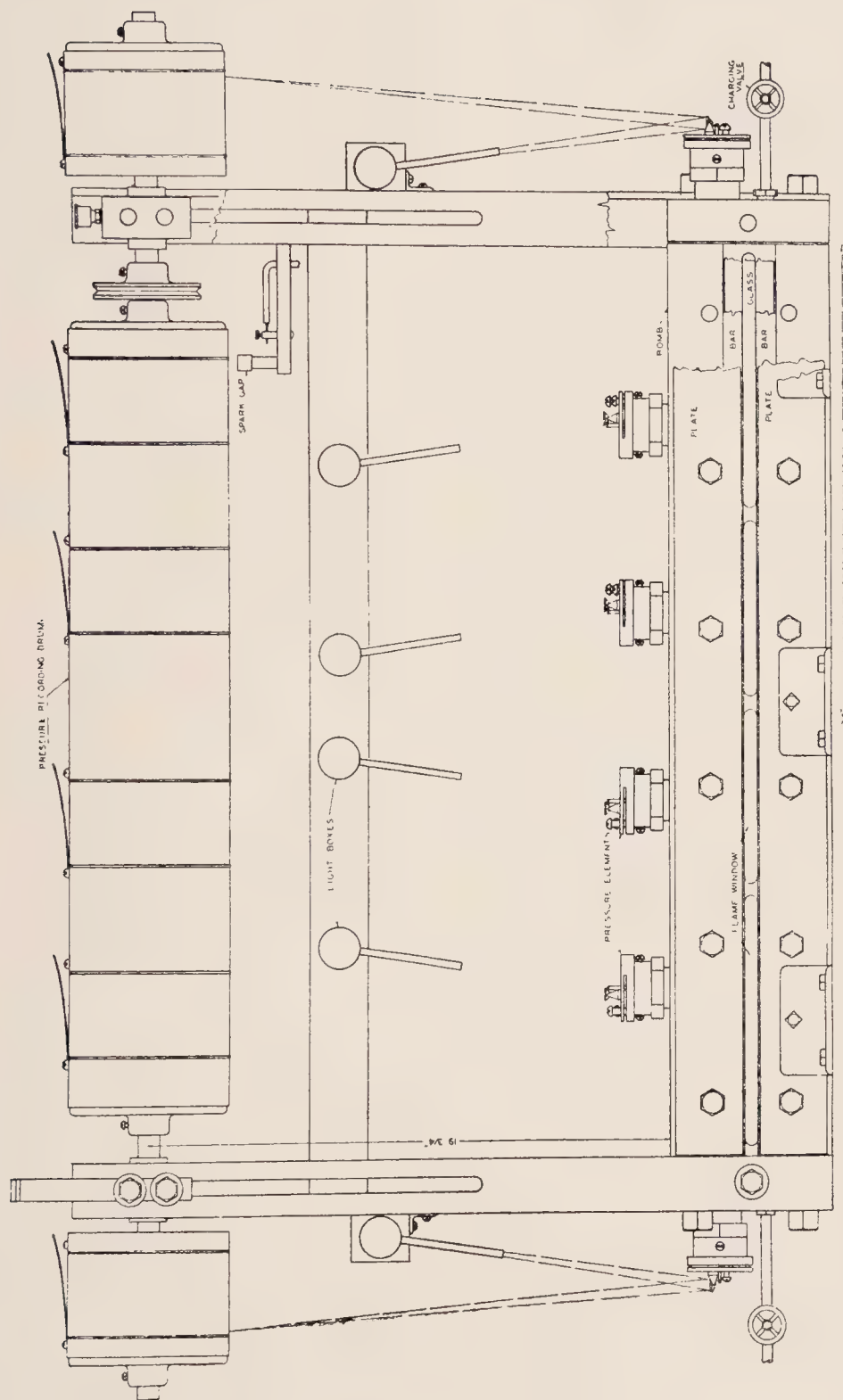


FIG. 2. Bomb and pressure recorder.

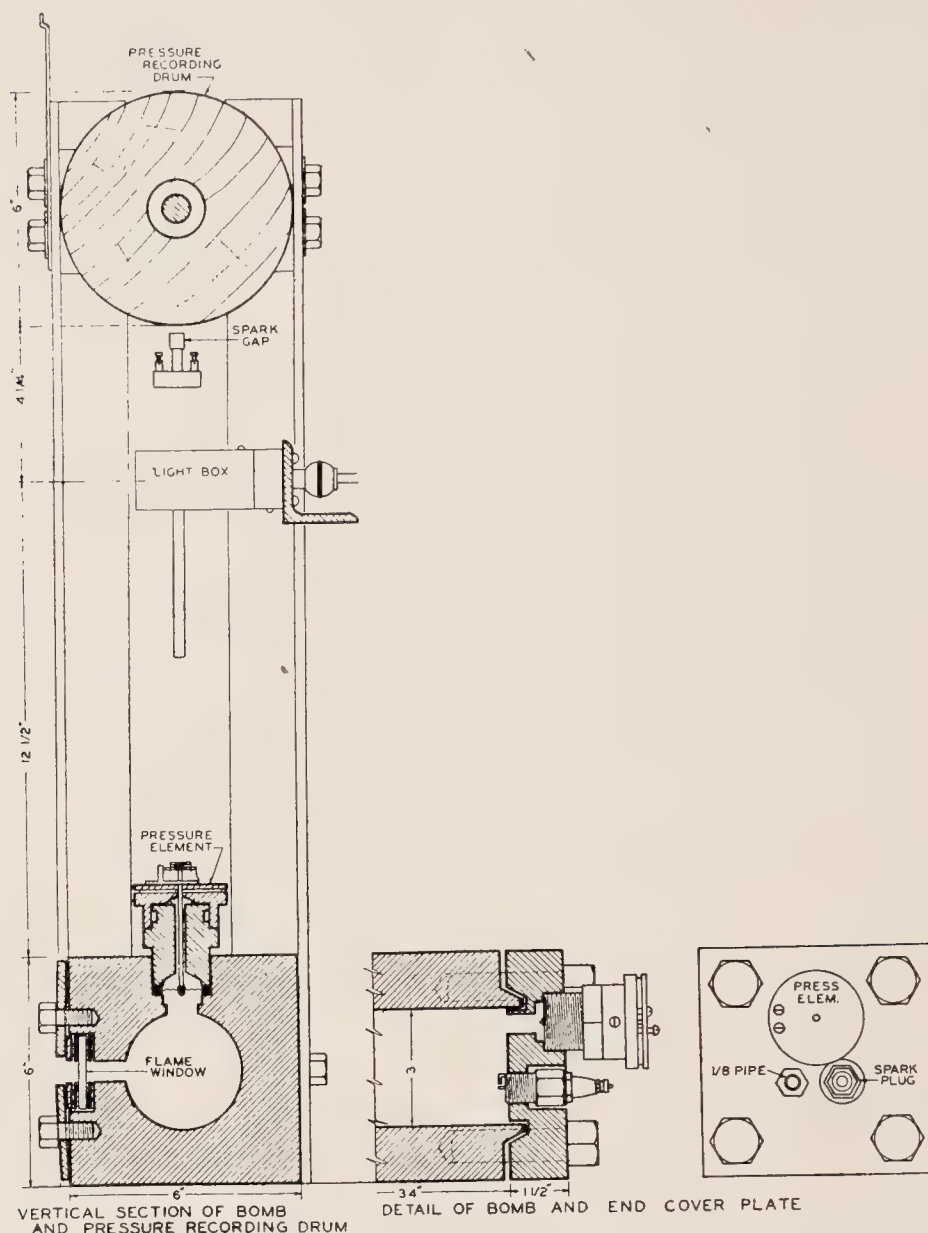


FIGURE 3

These bars projected about 0.32 cm (0.125 inch) above the face of the bomb and were held in place by two other bars of the same length, 6.4 cm (2.5 inches) wide and 0.63 cm (0.25 inch) thick, which were fastened to the bomb by means of cap screws. This arrangement, as shown in Figs. 2 and 3, was necessary in order that an even pressure might be brought to bear on the window to make it gas-tight without breaking the glass.

The bomb was constructed to accommodate six pressure elements, one on each end and four equally spaced along the top side adjacent to the flame window, as shown in Figs. 2 and 3. Details of the pressure elements will be taken up in conjunction with the pressure recorder.

Two holes were also drilled through each end plate and tapped with 1.27-cm (0.5-inch) pipe threads for spark plugs and charging valves.

Pressure-Recording Apparatus. The time-pressure cards were obtained photographically by deflecting a pencil of light by means of a movable concave mirror mounted on the pressure elements and brought to a focus on a revolving drum.

Lighting. The light was obtained from a 6-8 volt, 50 c.p., double-contact auto-headlight bulb overloaded to 12 volts. Each bulb was enclosed in an individual light box shown in detail in Fig. 7 and shown in position in Figs. 2 and 3. The light boxes were constructed so that the small beams of light coming from the shielding tubes could be individually adjusted to fall upon and just cover the mirrors of their respective pressure elements.

The four light boxes, furnishing light for the four pressure elements on the side of the bomb, were mounted by means of two screws each, to a

5.1-cm (2-inch) angle iron, which in turn was supported by two of the 5.1-cm (2-inch) angle-iron brackets holding the revolving drum. The angle iron could be raised or lowered for focusing the light, as reflected from the concave mirror, to a point upon the revolving drum. The light boxes for the two end pressure elements were mounted separately so that they might be focused individually. The distance from the mirror to the revolving drum is greater in the case of the end pressure elements and therefore requires separate adjustment of the light boxes.

Pressure Elements. The pressure elements were of the diaphragm type and so designed as to have minimum weight and movement to the moving parts, in order to reduce the lag of the indicator, due to the inertia of the moving parts, to as small a time interval as possible.

The pressure-element body was made from 5.7-cm (2.25-inch) hex bar cold-rolled steel (Fig. 5). The pressure-element head was made from 6.4-cm (2.5-inch) round bar cold-rolled steel.

The pressure-element head fitted down over the top of the element body and was held in place by two lock screws, pressing against the friction blocks, in the side of the element body. This arrangement allowed the element head to be rotated in either direction, so that the light could be adjusted to fall on the axis of the revolving drum, and locked in any position without raising or lowering the element head. To raise or lower the element head would throw the light out of focus.

A corrugated brass diaphragm 3.8 cm (1.5 inches) in diameter and 0.508 mm (0.020 inch) thick covered the bottom of the element body and was held rigidly in place when the element was screwed into the bomb. The diaphragm had an effective diameter of 2.54 cm (1 inch). A lead gasket was placed between the diaphragm and the bottom of the element recess in the bomb. This arrangement effectively sealed the element opening.

Diaphragms of different material and thickness were tried until one was obtained that would give the maximum deflection for the pressures developed without permanent deformation. The diaphragm used would withstand 7.03 kg per sq cm (100 pounds per square inch) without taking a permanent set.

The motion of the diaphragm was transmitted to a steel rod 9.5 cm (3 3/4 inches) long and 2.38 mm (3/32 inch) diameter which passed through a hole in the center of the diaphragm. The part of the rod passing through the diaphragm was threaded and a small brass nut on each side of the diaphragm allowed the rod to be fastened rigidly to it. The rod passed up through the center of the element body and through the

center of the element head, guided at the bottom of the body and at the top of the head. Around the top of the rod was a narrow groove into which fitted the small brass wing, V-notched, projecting from the bottom of the mirror mounting. This method of connecting the rod to the mirror mounting proved very satisfactory as it allowed a small change of angle of the wing with the rod without any play or lost motion at the joint. In this way the longitudinal movement of the rod was transmitted as angular rotation to the mirror mounting and thence to the mirror.

The mirror mounting was made of sheet brass 0.381 mm (0.015 inch) thick. A small steel rod 1.59 mm (0.067 inch) in diameter pointed at both ends was soldered to the bottom of the mirror support and served as the axis. The mirror mounting was held in place by the steel spring as shown in Fig. 5. The mirror was held in the mounting by small strips of brass, which were part of the mounting, and projected above the mirror at each corner and were bent down over it.

The mirrors were glass 1.27 cm (0.5 inch) square, 1.59 mm (0.067 inch) thick, with the concave side having a radius of curvature of 33 cm (13 inches).

Silvering Mirrors. The silvering of the mirror offered a considerable problem, as it was desirable that the reflecting side should be the same as that upon which the silver was deposited. This was necessary so that there would be no dispersion of light due to refraction, which would be the case if the light passed through the glass. The silver deposited by ordinary methods was thin and soft and would not long adhere to the glass without lacquering. Small ripples in the lacquer coat interfered with the focusing of the light and gave a corona effect around the central point of light, which registered on the photograph as a line with blurred edges.

These difficulties were overcome by silvering the glass by a special procedure. The ordinary silvering solutions were used but applied to the glass in the following manner: The glass was first cleaned in caustic solution and then in nitric acid, then rinsed in distilled water and rubbed with a chamois dipped in alcohol. While the glass was still wet the silvering solution was sprayed upon it, with considerable force, by an air jet. The silver nitrate and reducing solutions were allowed to mix and the reaction start before they entered the jet.

In this way a hard, dense, and very adherent silver deposit of any desired thickness could be built up upon the glass. This deposit required no protecting coat of any kind, for as it oxidized on the surface it could be repolished with fine jeweler's rouge.

Pressure-Recording Drum. The revolving drum

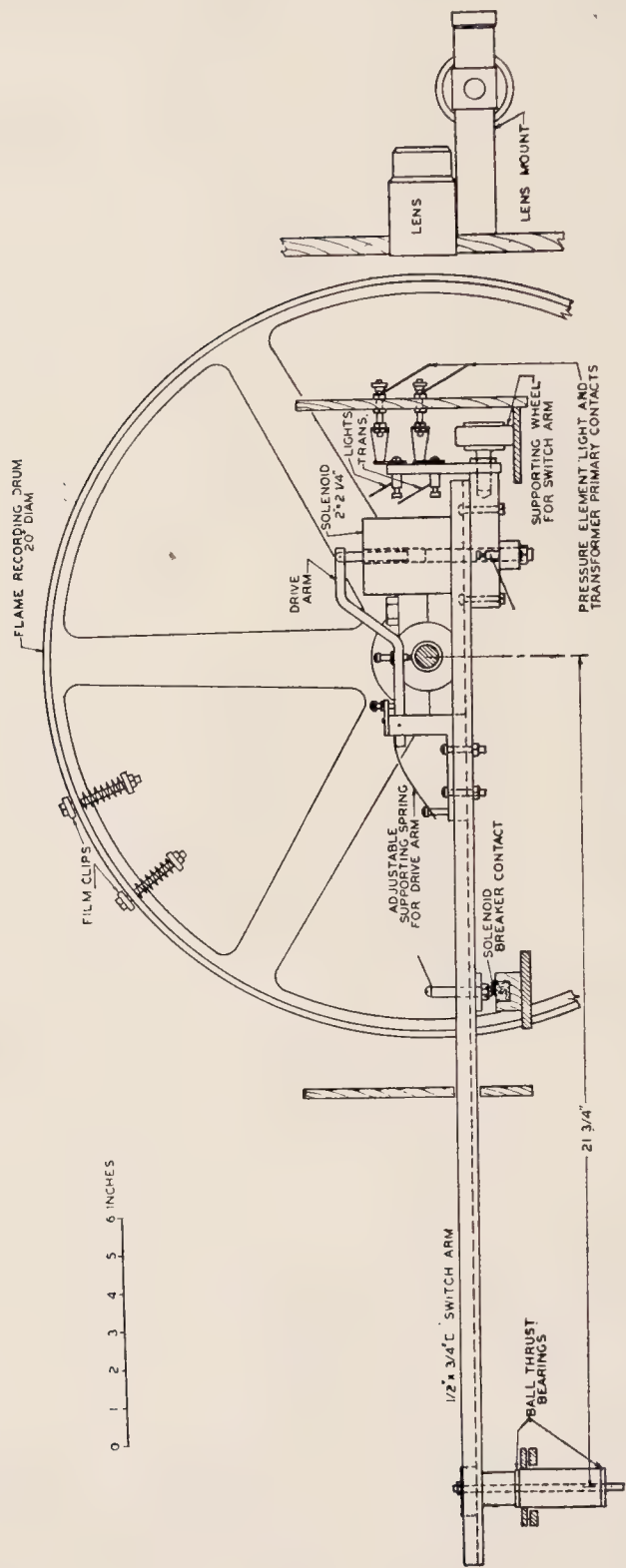


FIG. 4. Detail of automatic switch arm and flame drum.

for carrying the photographic recording paper was made of solid ply maple 15 cm (6 inches) in diameter and mounted as shown in Fig. 2. Wires 2 inches apart were drawn around the drum in grooves to hold them in place. These wires served as guides for the recorder paper. The paper was held to the drum by means of spring wire clips sunk in a groove cut parallel with the axis of the drum. The lights of the pressure elements were so adjusted that they all fell upon a line parallel with the axis of the drum. The grooves, containing the recorder paper clips, were used for this purpose.

The drum was driven by a 1/4-horsepower electric motor, mounted upon the floor to reduce vibration. The power was transmitted by a 0.63-cm (0.25-inch) round leather belt to a jack shaft and from there to the drum.

Flame Recorder. The flame travel was recorded photographically upon panchromatic film by means of a rapid lens.

Flame-Recording Drum. The flame drum (Figs. 1 and 4) for carrying the motion-picture film was

made from a cast-iron belt pulley, 50.8 cm (20 inches) in diameter and with a 10.1-cm (4-inch) face, mounted upon a pipe frame entirely separate from the bomb. The pipe frame was securely braced with heavy angle iron and fastened to the concrete floor in eight places with 1.27-cm (0.5-inch) expansion bolts.

The face of the flame drum was ground, after it was mounted into position, until it was true with its axis of rotation within 0.0127 mm (0.0005 inch) when turning at 700 rpm. This accuracy was necessary so that the photographic film would not be carried out of focus with the lens. Two grooves 3.5 cm (0.38 inch) apart were cut in the face of the flame drum. Wires were drawn around the drum, held in position by the grooves, which served as guides in placing the film on the drum. Two brass clips, which were clamped down by coiled springs below the face of the drum, held the film in position on the drum. The drum was very carefully balanced until no vibration was perceptible, as this vibration would affect the flame photograph.

Lens. An Ultrastigmat lens F:1.9, in a microm-

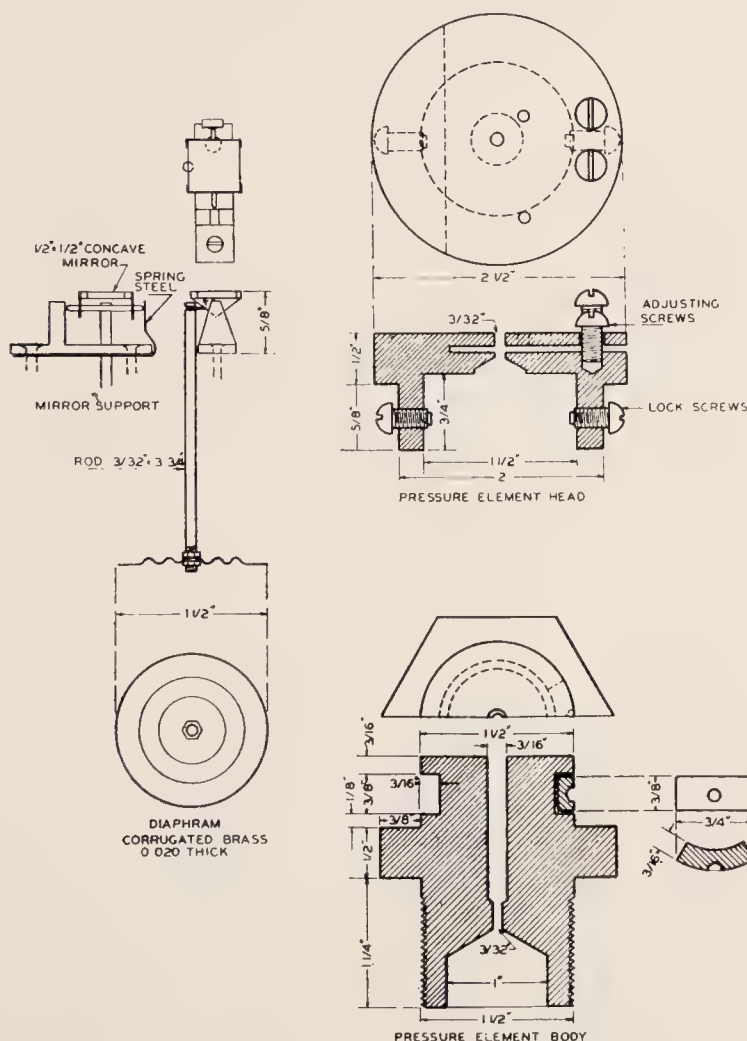


FIG. 5. Detail of pressure element.

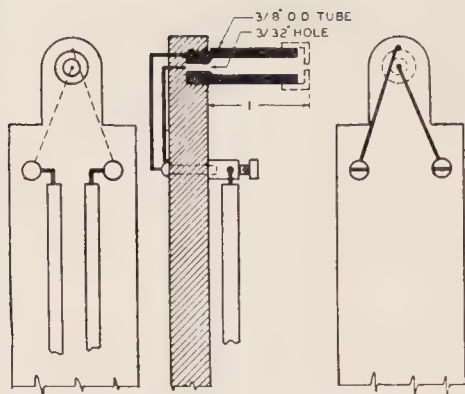


FIG. 6. Detail of spark gap.

eter mount, was mounted in front of the flame drum as shown in Figs. 1 and 4. A rack and pinion at the bottom of the lens mounting was used for the coarse focusing of the lens. The micrometer mount was used for the fine focusing of the lens.

The flame drum was entirely shielded by a wooden and metal box with a hinged top to allow access for placing and removing the film. The focusing was done by means of a small hole through the shield which allowed a view of the surface of the drum in back of the lens. This hole was covered by a slide of sheet metal.

The shaft of the flame drum was supported by three heavy block bearings (Fig. 1) and driven by means of a flat belt from a 1/4-horsepower motor mounted on the floor.

Wiring and Timing Mechanism. High-voltage spark gaps, fed from a small transformer, were used to establish time intervals and time relations between the pressure drum and the flame drum. The same transformer was also used for firing the charge in the bomb. The transformer was supplied with 60-cycle alternating current.

The high-voltage output of the transformer would jump the gaps only when a sufficiently high voltage had been reached to break down the resistance of the gaps. This, of course, would occur when the voltage was rising or at its peak, depending upon the width of the gaps, or with a frequency of 120 per second when 60-cycle current was used. Therefore, when this spark was photographed on moving film and paper it registered a dot or group of dots every 1/120 of a second.

Where two spark gaps are connected in series, one placed so as to register on one film traveling at one speed and the other to register on another film traveling at a different speed, the time relations between the two films is definitely established, because the sparks jump both gaps at the same instant, neglecting of course the

extremely small interval required for the travel of the electricity from one gap to the other.

The type of spark gap used is shown in detail in Fig. 6. The spark jumps between the end of the wire and the inner edge of the tube. The gaps are mounted on blocks of Bakelite. The tube arrangement prevents fogging of the film and paper by diffusion of the light from the spark.

One spark gap was mounted directly below the pressure drum and fastened to the angle irons supporting the drum. The light from this gap was registered on the same photograph as the pressure from the pressure element below it (Figs. 1, 2, and 3). The other spark gap was mounted in front of and at the center of the flame window and faced the photographic lens so as to register on the flame photograph (Fig. 1).

This position of the gap brought it directly in front of one of the bridges across the flame window. The bridge across the window shut off the light of the flame at this point and therefore made the photograph of the spark easily discernible.

Because of the high voltage used, the capacity effects of the bomb and wiring were great enough to cause sparks to jump across the gaps when one side of the secondary transformer circuit was open and only the primary closed. A condenser of sufficient capacity to absorb this discharge was placed across both gaps. The condenser also absorbed and stored energy while the voltage was building up in the transformer and lengthened the time necessary for the voltage to reach a sufficiently high potential for jumping the gap. When the resistance of the gap was broken down, high-frequency oscillating currents in the condenser circuit rapidly dissipated the energy of the charge, so that there would be fewer but more intense discharges between each change in direction of the current in the transformer circuit.

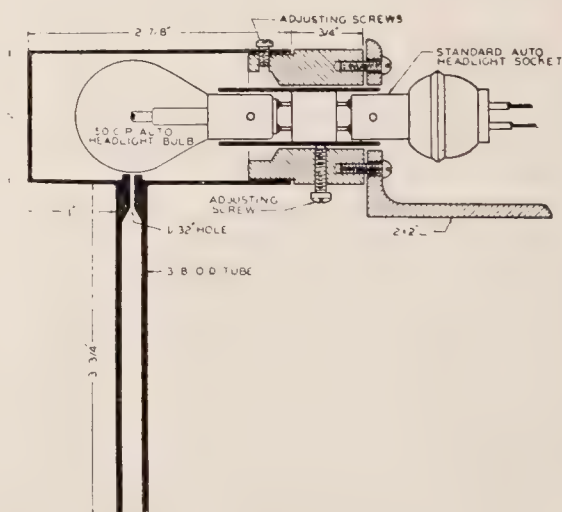


FIG. 7. Detail of light box.

A very effective condenser was made from glass tubing and mercury. A 3-mm glass tube 60.8 cm (24 inches) long, sealed at one end, was placed inside a 7-mm glass tube 55.8 cm (22 inches) long also sealed on one end. The 3-mm tube and the annular space between the two tubes were filled with mercury. The two columns of mercury acted as two plates of a condenser. Units of this type were added until the condenser had the desired capacity. The advantage of this condenser lay in its ease of construction, replacement when punctured, and adjustment of capacity.

The rest of the firing and timing mechanism may best be described by following through the wiring diagram as shown by Fig. 1. By closing the switch of the 110-volt a-c line (lower right-hand corner of Fig. 1) the motors driving the two drums are started and the voltage is also applied to one side of the pressure-element light circuit, through a resistance to control the voltage, and to one side of the primary winding of the transformer. The other lead to the lights and transformer terminates in two small brass contact plates at the end of the automatic switch arm.

After the drums are up to speed, the 110-volt d-c switch (also in lower right-hand corner of Fig. 1) is closed, which actuates the solenoid mounted on the switch arm. The details of construction of the switch arm are shown in Fig. 4. The solenoid pulls a pin into a screw which is cut in the shaft of the flame drum. This screw, with a pitch of two threads per inch, carries the switch arm across the light and primary transformer contacts. Contact is first made with the light circuit. The primary transformer contact is closed when sufficient time has elapsed for the lights to attain full intensity.

One side of the secondary winding of the transformer is grounded to the bomb. The other side leads first through the two-timing gaps and then to the ring of the high-voltage distributor which is mounted on the end of the shaft of the flame drum. The shaft, turning clockwise, brings the small segment on the face of the distributor into contact with the outside brush shortly after the primary circuit of the transformer is closed. When the small segment of the distributor comes in contact with the outside brush, the secondary circuit of the transformer is closed through the spark plug and the charge in the bomb is fired. A condenser, similar to the one previously described, was placed across the spark-plug gap to prevent the firing of the charge by capacity discharge. The small segment of the distributor remains in contact with the brush a little over $1/120$ second. Therefore, the size of the segment depends on the speed of the flame drum. When the outside segment leaves the outside brush, the inside

segment comes in contact with the inside brush. The line from the inside brush is grounded directly to the bomb. In this way the spark plug is shorted after one or possibly two discharges across the gap. This arrangement was used so that additional impulses would not be added to the burning mixture by additional sparks jumping the gap in the spark plug. The inner segment of the distributor was of such length that the total time required for the passage of both segments under both brushes would be slightly less than the time required for one revolution of the pressure drum. In this way overlapping of the timing dots on the pressure cards was avoided.

By the time that the inside segment of the distributor has left the inside brush, the light and primary transformer contacts have passed across the plates on the end of the switch arm, thus turning off the lights and breaking the primary circuit of the transformer. The switch arm continues to move until the d-c circuit, actuating the solenoid, is broken by the brush which is carried on the switch arm, passing off of the switch block mounted beneath the switch arm.

Operation

After the bomb chamber was thoroughly flushed with oxygen, the fuel was measured into the charging valve by means of a pipet, and blown into the bomb with oxygen. Initial pressure was atmospheric.

Fuel Used. Carbon disulfide was the fuel used for the preliminary work. This compound, on burning, gave a bright luminous flame which was easily photographed. For each charge 0.71 cc of carbon disulfide liquid, equivalent to 262 cc of vapor, was used. If air instead of oxygen had been used, this size charge would have made a theoretical mixture.

Pressure-Recording Paper. The photographic paper was next placed in position upon the pressure drum. The paper used for this purpose was Recorder No. 1, furnished by the Eastman Kodak Company. The paper was cut into strips 7.62 cm (3 inches) wide and 50.8 cm (20 inches) long. This length allowed lapping on the drum so that a continuous photograph would result.

Flame-Recording Film. The photographic film was next fastened to the flame drum. Standard unperforated panchromatic motion-picture film was used for this purpose. This was cut into lengths 152.4 cm (60 inches) long and had small tabs of canvas cemented to the ends. The teeth on the bottom of the film clips were able to obtain

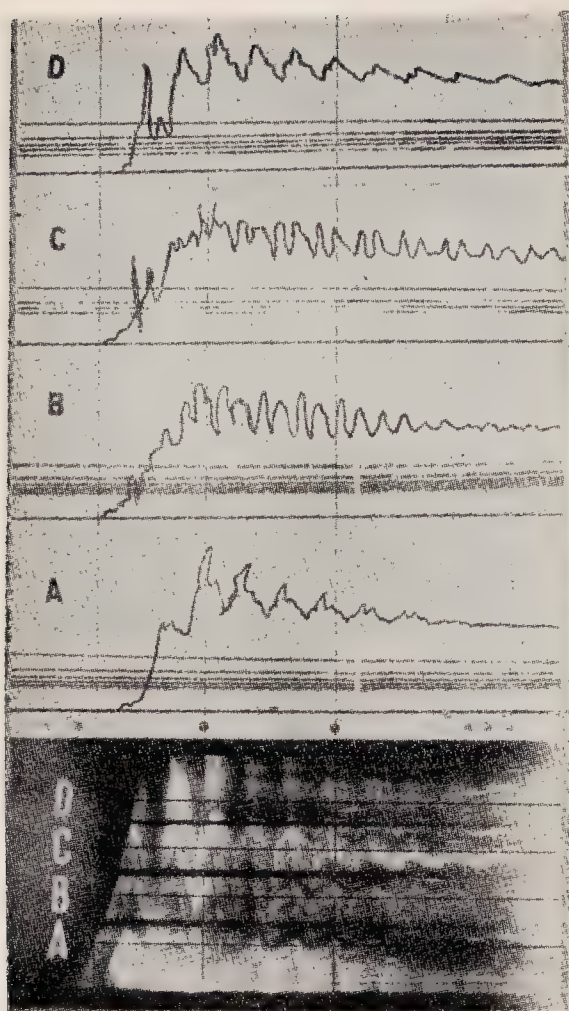


PLATE I

Flame and Pressure Record

a better grip upon the canvas than they could upon the film itself. In this way the film could be drawn more tightly about the flame drum. If the film was not tight, the centrifugal action of the drum would throw the film away from the surface of the drum and so out of focus with the lens.

Safe Lights. It was of extreme importance to observe the correct manipulation of the dark-room safe lights. This necessity arose because the recorder paper was sensitive to green light but not sensitive to red, while in the case of the panchromatic film the conditions were reversed. Thus the same light could not be used for both the film and paper. By placing the recorder paper first and then shielding the pressure drum with a canvas curtain while the panchromatic film was being placed on the flame drum, this difficulty was overcome.

Exploding the Mixture. The apparatus was now ready for operation. This part of the procedure was very simple. The apparatus was so designed that the personal element was practically elimi-

nated from the operation. The a-c switch was first closed and the drums allowed to come up to speed, then the d-c switch was closed. After the explosion, and after the pressure-element lights had gone out, the a-c and d-c switches were again opened and the operation was completed.

Developing the Photographic Records. The same precaution as to lights was observed while developing the paper and film. The paper was developed by nepara solution and the film by hydroquinone. The complete operation, including the developing after the paper and film were cut, required about one-half hour.

After drying, the photograph of the flame was enlarged to such an extent that its time axis was the same as that of the time-pressure cards. This was accomplished by enlarging until the timing dots made by the electric spark on the flame photograph could be superimposed upon the timing dots on the time-pressure cards and exactly coincide. In this way the time relation

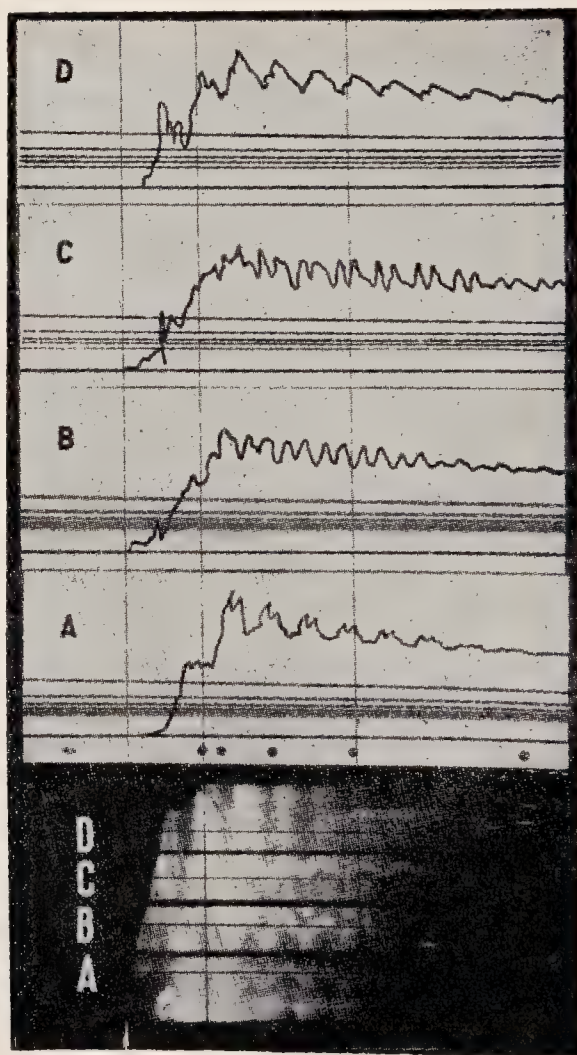


PLATE II

Flame and Pressure Record

between the photographs taken upon the two drums traveling at different speeds was definitely established.

Results

Interpretation of Data. The results of two check explosions so obtained are shown by Plates I and II. The lower photograph of each plate is the enlarged photograph of the flame. The time axis is horizontal and the vertical axis represents the length of the bomb. The three wide black horizontal lines through the photograph were made by the bridges across the window, shutting off the light of the flame at these points. The four narrow black horizontal lines marked A, B, C, and D show the positions occupied by the four pressure elements along the side of the bomb.

The four time-pressure curves above the flame photograph, marked A, B, C, and D, are reproductions of the four time-pressure cards taken along the sides of the bomb in the positions above indicated. The end-pressure elements were not used, as this investigation was primarily concerned with the pressures developed by the flame as it is propagated through the explosive mixture.

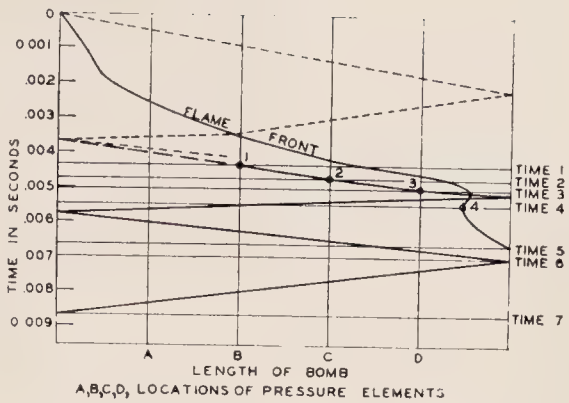


FIG. 9. Sound waves and pressure waves accompanying the flame propagation.

It should be noted that the timing dots shown on pressure card A correspond with the dots shown in the center of the flame photograph. The first dot at the left represents the spark that fired the charge. The narrow vertical lines across the plate were drawn to align the five photographs.

Inspection of the time-pressure curves B, C, and D, shows that there was a sharp rise and fall of pressure before the maximum pressure was attained. This sharp rise and fall of pressure under indicator C took place at a later time and was of a greater magnitude than that indicated by B, while the rise and fall of pressure indicated at D took place at a later time and was of a greater magnitude than that indicated by C.

The plot of the pressures throughout the length of the bomb as indicated at A, B, C, and D at the instant at which the sharp rise of pressure at B had reached its maximum is given by Chart 1 of Fig. 8. This shows that at that instant when the greatest pressure along the bomb was in a position opposite indicator B, the flame front (F) had advanced past indicator C.

Figure 9 is a tracing of the flame photograph of Plate I rotated through 90 degrees so that the horizontal axis represents the length of the bomb and the vertical axis represents time with zero time at the top. Time 1 represents the instant at which the pressures were taken for Chart 1, Fig. 8.

Chart 2, Fig. 8, is similar to Chart 1 except that it represents the pressure distribution at time 2 (Fig. 9), the instant at which the sharp rise and fall of pressure given by indicator C had reached its maximum. The flame front (F) had progressed to a position opposite indicator D.

Chart 3, Fig. 8, represents the pressures along the bomb when the rapid rise and fall of pressure indicated at D had reached its maximum (time 3, Fig. 9). The flame front had progressed

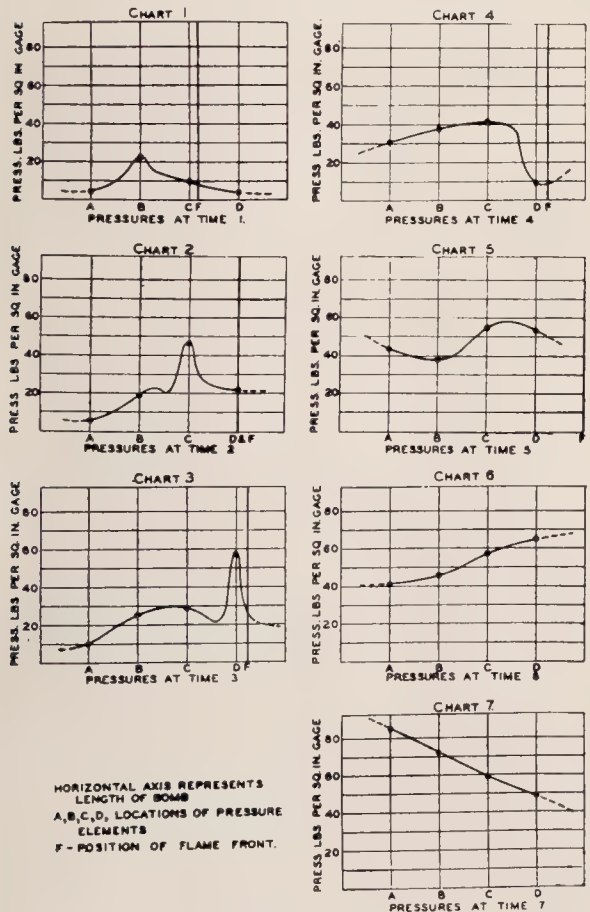


FIG. 8. Pressure distribution.

to a position about half way between indicator *D* and the end of the bomb.

Chart 4 gives the pressures along the bomb when the flame had fallen back to its point of maximum recession given as time 4, Fig. 9.

Chart 5 shows the pressures along the bomb when the flame front had reached the end of the bomb (time 5, Fig. 9).

Charts 6 and 7 show the pressures along the bomb at later time intervals (times 6 and 7, Fig. 9).

Charts 1, 2, and 3 show that a peak of pressure travels through the gas in back of the flame front and that this peak of pressure was traveling at a higher velocity than the flame front. The curve drawn through points 1, 2, and 3 of Fig. 9 shows that the peak of pressure, or pressure wave, was increasing in velocity, and that it overtook the flame front at the same time that the flame halted. It is safe to assume that this pressure wave did not stop at the flame front but continued on ahead of the flame to the end of the bomb and was reflected therefrom.

As this pressure wave passes from the high-temperature medium behind the flame front into the relatively cool gases ahead of the flame, its velocity will probably decrease. In Plate I, and also Fig. 9, the distance that this pressure wave travels through the relatively cool gases ahead of the flame front is so small that no definite conclusions may be reached from the experimental data as to whether this pressure wave continues with the same or with a decreased velocity. Comparison of the flame photograph with the time-pressure curves (Plate I) and the charts of Fig. 8 clearly indicates that this pressure wave was reflected from the end of the bomb and entered the flame front at the point of recession of the flame. It then continued through the burning gases, being supported by the increase in the rate of combustion that it promoted. Upon reaching the firing end of the bomb it was again reflected and traveled back the length of the bomb, reaching the far end at approximately (slightly later than) the same time as the flame front. That a pressure wave travels the length of the bomb and back is substantiated by Charts 6 and 7 (Fig. 8) and also by the flame photograph.

This pressure wave traveling back and forth the length of the bomb caused variations in pressure throughout the bomb during the entire burning period, as shown by Plates I and II. These pressure curves (also Charts 6 and 7, Fig. 8) show that, when a peak of pressure occurs at one end of the bomb, a trough or low pressure occurs at the other.

These pressure curves and the flame photograph show that the peaks of pressure occurred when the flame was at maximum intensity,

which point was just after the incandescent particles had changed direction.

Velocity of Reflected Wave. After the pressure in the bomb reached a maximum, the reflected pressure wave traveled at a constant velocity. This velocity is very easily measured by means of the contact prints of the original flame negatives. Scaling the photograph shows that the wave traveled the length of the bomb ten times in 2.032 cm (0.8 inch) on the circumference of the flame drum. That is equivalent to 425 cm per cm (425 inches per inch) of film. The flame drum has a circumference of 159.5 cm (62.8 inches) and travels at 63 rpm. Therefore, 1 cm (1 inch) of film is equivalent to 0.00657 second (0.0167 second). This would give the wave a velocity of 646 meters (2120 feet) per second.

It is interesting to note what would be approximate velocity of a sound wave traveling through this mixture under the same conditions. From the average pressure rise of 50 pounds gage, the approximate average temperature of the mixture can be computed as follows:

Average pressure rise, 3.515 kg/sq cm (50 psi)
Total average pressure, 4.554 kg/sq cm (64.7 psi)
Temperature corresponding to this pressure:

$$(294^{\circ}\text{K} \times 4.554) - 1.003 = 1294^{\circ}\text{K}$$

$$(530^{\circ}\text{A} \times 64.7) - 14.7 = 2330^{\circ}\text{A.}$$

The velocity of sound in oxygen at 0°C (32°F) is given by Dulong as 317.2 meters (1041 feet) per second. The velocity of a wave in a gaseous media varies directly as the square root of the absolute temperature therefor:

$$V/\sqrt{T} = 317.2/\sqrt{294} = V/\sqrt{1294}$$

$$(V/\sqrt{T} = 1041/\sqrt{530} = V/\sqrt{2330})$$

$$V = 664.6 \text{ meters per second}$$

$$(V = 2180 \text{ feet per second})$$

The velocity of a sound wave in this mixture would, therefore, be approximately 664.6 meters (2180 feet) per second, which is very close to the actual velocity of the reflected wave shown in the photographs.

A sound wave set up by the igniting spark would travel ahead of the flame front, be reflected from the far end of the bomb, and meet the flame front when it had progressed to a position opposite pressure element *B* (Plate I). This sound wave, continuing on through the burning mixture at a higher velocity due to the increased temperature and pressure of the burning gases, would, after reflection from the firing end of the bomb, coincide with the observed pressure wave following the flame front. We have not yet established whether or not the coincidence of the reflected sound wave with the pressure wave is fortuitous.

At the ends of the bomb a trough or low pressure is found where the particles change their direction of motion from away from the end to toward the end of the bomb, and a crest or peak of pressure is found where the particles reverse their direction from toward the end to away from the end of the bomb.

Discussion

Sound Wave from Igniting Spark. When the sound wave set up by the igniting spark meets the flame front, part of the wave will continue on into the burning gases and part will be reflected from the flame front. The wave reflected from the flame front will tend to support the flame and carry the flame with it. The flame photograph (Plate I and Fig. 9) shows that there is an increase in velocity of the flame front as it progresses from the position of contact with the sound wave (under indicator B) and that this velocity is the velocity of sound in the unburned gas.

The above interpretation does not agree with Dixon's idea that the sound wave set up by the igniting spark is the direct cause of the halt of the flame front, but rather, as will be indicated, may be the indirect cause of the halt of the flame front.

Halt of Flame Front. The sound wave set up by the igniting spark, which passes into the burning mixture after meeting the flame front, will travel with an increased velocity due to the higher temperature and pressure in the burning gases. As has been indicated, this sound wave after reflection from the firing end of the bomb, almost coincides with the observed pressure wave following the flame front. As stated by Dixon, the sound wave, which is a pressure wave of low amplitude, might cause some increase in rate of combustion in the wave crest with consequent increase in the amplitude of the wave itself. If the coincidence of the sound wave and the pressure wave is not fortuitous, this might be an explanation of the source of the pressure wave following the flame front. However, no increase in rate of combustion was noted in any flame photograph as the sound wave reflected from the end of the bomb entered and passed through the burning gases.

This pressure wave as it increases in amplitude and as the medium through which it is passing increases in temperature and pressure, travels with increasing velocity. This wave, which is traveling with a greater velocity than the flame front, must overtake the flame front if the explosion chamber is of sufficient length. As has been previously shown, this pressure wave does

overtake the flame front at the position at which the flame is halted.

The trough or low-pressure area following the peak pressure of the wave tends to decrease the rate of burning. The movement of the particles toward the rear of the flame and the decreased rate of burning cause the apparent halt and recession of the flame front.

Woodbury, Lewis, and Canby² have suggested that the pressure built up ahead of the flame is the cause of the halt of the flame front. The results here presented show that a pressure ahead of the flame front is the cause of the halt of the flame, but that the origin of this pressure is not that suggested by them.

Pressures Accompanying Flame. As has been previously shown (Fig. 8), the pressures ahead of the flame front, although increasing as the flame progresses, are of much lower order of magnitude than those immediately following the flame front. Also, when the pressure ahead of the flame front becomes greater than the pressures behind the flame front, the flame is halted. This evidence is directly contrary to the theory presented by Midgley³ that the pressure ahead of the flame front must be greater than that behind the flame front if the flame is to be propagated into the unburned mixture.

Maximum Pressure Development as Related to the Flame. Previous investigators have disagreed as to the time of maximum pressure development as related to the inflammation of the mixture.

Woodbury, Lewis, and Canby² state that "the instant of maximum pressure development coincided with that of total inflammation of the gas." They present no conclusive evidence for their statement.

Dixon,¹ in discussing this point, says

If the authors [Woodbury, Lewis, and Canby] mean by total inflammation the fact that the flame has spread from end to end of the vessel and that the whole column of gas is visibly alight, it may happen that the pressure is greatest at that moment, but in many cases, and I believe in most instances, the greatest mean pressure occurs after the flame has completely filled the vessel.

Hopkinson⁴ proved by actual temperature and pressure measurements that the flame might fill the entire chamber some time previous to the attainment of maximum pressure.

Nagel⁵ developed an elaborate mathematical analysis of rate of flame travel based on the assumption that the time of maximum pressure corresponds to the time of complete inflammation.

Wheeler,⁶ working with a spherical bomb,

reported that the time of total inflammation corresponded with that of maximum pressure development. He recorded the time interval between ignition of the charge and passage of the flame at a point 7.5 cm from the point of ignition by means of the fusion of small copper wires placed at these points. This involved the assumption that the flame front produced sufficient heat to fuse the wire and that there was no time involved in the fusion. Also the fact that he recorded the passage of the flame at only one distance from the point of ignition would involve the assumption that the flame front traveled at a constant velocity.

Inspection of Plates I and II led us to agree with Dixon and Hopkinson that the time of maximum pressure may occur after the time of total inflammation, because at the time of total inflammation the mixture generally contains gases that are not completely burned by the initial flame.

Detonation Wave. As previously stated, our experimental results show that a pressure wave of high amplitude travels through the burning gases in back of the flame front, and that owing to its greater velocity it overtakes the flame front if the explosion chamber is of sufficient length. We also have shown that when the pressure wave overtakes the flame front the flame is halted.

In the case of more rapidly burning mixtures than here reported, a condition might result due to the higher temperatures developed, in which the pressure wave following the flame front would overtake the flame front at a time when its velocity would be only slightly less than

that of the pressure wave. Under these conditions the flame front might be carried forward on the crest of the pressure wave instead of falling behind and being halted by it. This may be the mechanism by which the detonation wave is set up.

Conclusions

This paper is intended primarily to show the usefulness and possibilities of the apparatus here described. The experimental results so far obtained indicate that:

1. As the flame propagates through the explosive mixture, a pressure wave is set up in the burning mixture behind the flame front and travels at a greater velocity than the flame front.

2. The pressure in the crest of this wave behind the flame front is greater than the pressure in the flame front or in the unignited mixture ahead of the flame.

3. The halt and recession of the flame front is caused by the pressure wave, which follows the flame front at a greater velocity, overtaking and passing through the flame front.

4. The maximum pressure, in the case of mixtures promoting after-burning, is developed some time after total inflammation of the charge.

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SOME FLAME CHARACTERISTICS OF MOTOR FUELS

G. B. MAXWELL AND R. V. WHEELER

Department of Fuel Technology, Sheffield University, England

In order to obtain some information as to the cause of the "pink" or knock of motor fuels, a photographic study has been made of the movement of flames, simultaneously with measurements of the development of pressure, during the explosion of the charge in an engine cylinder. Explosions of mixtures of pentane and air and benzene and air, at various temperatures and pressures, and of various blended mixtures of benzene and pentane, and of ethyl ether with pentane and air, have been studied. Suggestions are made for the suppression of pinking, and on the basis of these studies the differences between pinking and non-pinking explosions are pointed out.

At present there is a deadlock in the design of light, high-speed internal-combustion engines for automobile and aircraft use. The effect of increased compression in increasing efficiency is thoroughly realized. So also is the attendant evil, "pinking," to which increased initial compression may lead.

Designers are prepared to supply high-compression engines if the common run of motor fuels can be used in them. Ricardo,¹ for example, paying due regard to foundry and machine-shop difficulties, weight and mechanical efficiency, considers that an engine having a 7.5 to 1 compression ratio can readily be put on the market. Unfortunately, even the most carefully blended petrols pink in the average engine of 2.5- to 3-inch bore when the compression ratio exceeds 5 to 1; the amount of "dope" that would have to be added to make possible a 7.5 to 1 ratio would be excessive and would lead to secondary complications.

"Pinking," "knocking," or "detonation," as it is variously called, has thus come to be a serious problem to the fuel producer. Intensive research has led to improvements in the design of engines and the blending and "doping" of fuels, but the cause of the trouble is still not clear. The most prevalent view is that the "pink" is due to a sudden development of pressure on inflammation of the unburnt residue of charge which has been compressed and heated by contact with the portion already ignited. The violence of the effect—it must be assumed that there is a very sudden increment of pressure—has been attributed by different investigators to the activation of the unburnt residue either by ionization, radiation, or preliminary oxidation of liquid nuclei leading to the formation of explosive organic peroxides. These various theories have led to a considerable amount of investigation into compression ignition and "igniting temperatures" of fuel-air mixtures and into the ionization and radiation phenomena accompanying combustion.

The writers have long considered that a solution of the problem should be obtainable through a

photographic study of the movement of flame, simultaneously with measurements of the development of pressure, during the explosion of the charge in an engine cylinder. Some of their preliminary experiments have already been reported.² This paper gives a résumé of the earlier results together with more recent work. In order to simplify photographic arrangements and to control and vary the initial conditions more readily, attention has thus far been confined to explosions within a closed cylinder, without a moving piston. The cylinder was of stainless steel, 6 inches (15 cm) internal diameter. The internal length was normally 15 inches (38.1 cm), but this was reduced to 10 inches (25.4 cm) in certain experiments by the use of a special bucket-shaped end plate. The moving flame was photographed through a glass window fitted into a slit in the cylinder wall and the sensitive Lumière paper was attached to a revolving drum. On the same paper was obtained a continuous record of the development of pressure by means of an optical pressure indicator of the diaphragm type, similar in construction to the Rice manometer used by the United States Bureau of Mines. This was fitted at the center of one end plate and the spark plug was carried centrally by the other end plate.

Combustion of a Pinking Fuel—Mixtures of Pentane and Air

It is known that the paraffins are the most readily pinking constituents of petrol. Pentane (isopentane) was chosen to represent this class, since it is sufficiently volatile to give mixtures with air over the inflammable range at room temperatures and can really be obtained pure.

Initial Pressure 1 Atmosphere; Initial Temperature 15°C. At this pressure and temperature the range of inflammable mixtures of pentane and air is between 1.5 and 4.5 per cent pentane by volume (26.5 to 1 and 8.5 to 1 air-pentane by weight). The theoretical mixture for complete combustion contains 2.55 per cent pentane by



FIG. 1. Pentane 2.85 per cent.
1 atm., 15°C. Nonpink

volume (15.4 to 1 air-pentane by weight), while the mixture which gives the greatest and most rapid development of pressure contains about 3 per cent—(13 to 1 air-pentane by weight).

When mixtures containing from 2 to 3.4 per cent pentane by volume are ignited under the conditions of the experiments, a flame passes through the charge with an accelerating speed until it is slightly beyond the midpoint of the cylinder. Here the flame is checked and then travels at a slower and nearly uniform rate until it reaches the end plate (Fig. 1). Up to the point of check the flame is shaped like a blunt-nosed hollow shell; it then appears momentarily as a flat disk and, on continuing its now retarded movement, the outer edges, near the cylinder walls, lead the way. The flame appears to have been turned inside out. A faint glow appears throughout the products of combustion, behind the flame, at the moment of check. This glow then dies away slowly from the point of check towards the igniting plug. A more actinic afterglow, somewhat diffuse, appears throughout the cylinder shortly before, and continues for some time after, the initial flame is extinguished.

The pressure records show an even rise, except for a check corresponding to the flame check, up to a maximum. This is attained at about the moment that the central, rearmost portion of the flame is extinguished at the end plate. All such explosions are inaudible.

For mixtures containing more than 3.5 per cent pentane by volume the same remarks apply,

except that in very rich mixtures (more than 4 per cent pentane) the flame front is very ill-defined and its speed nearly uniform throughout its travel. Mixtures containing approximately 3.5 per cent pentane (11 to 1 air-pentane by weight) give an audible explosion and certain unusual features in the flame movement are observed. Shortly before the retarded flame reaches the distant end plate it commences to vibrate and accelerate. The pressure records show simultaneous vibrations of the same frequency. There is little or no afterglow in the wake of the flame until it strikes the end plate, at which moment a slight glow travels at an exceedingly high speed throughout the cylinder.

Initial Pressure Greater than 1 Atmosphere; Initial Temperature 15°C. The explosion of mixtures of pentane and air containing less than 3.2 or more than 3.8 per cent pentane by volume is not affected to any extent by increased compression to 2 or 3 atmospheres, absolute. The afterglow near the end of the flame travel is somewhat more intense, but the mean flame speeds are not appreciably altered and the explosions are inaudible. Mixtures within this range (3.2 to 3.8), however, all give audible explosions and flame vibrations at 2 atmospheres initial pressure. The explosions are very shrill, and at the moment when the accelerating, vibrating flame is extinguished at the far end plate a very intense glow travels throughout the cylinder. A considerable pressure increment is shown by the gage at this moment, and in some instances the

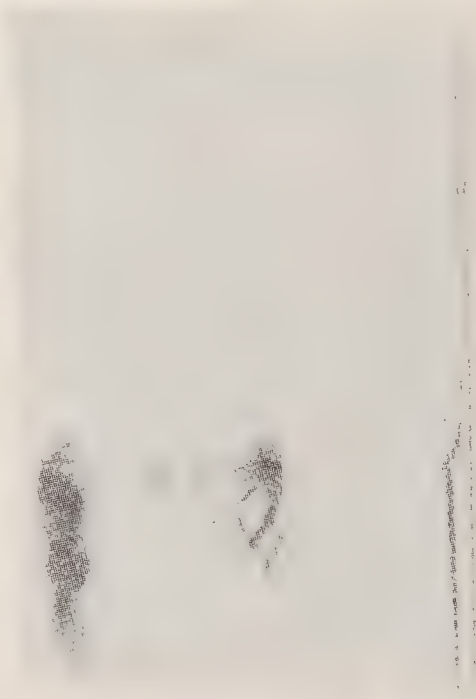


FIG. 2. Pentane 3.3 per cent.
2 atm., 15°C. Pink

records leave little doubt that a shock wave has struck the diaphragm. The effect of the compression is most marked in the 3.5 per cent mixture, a result which might be expected from the experiments at 1 atmosphere (Fig. 2). At 3 atmospheres initial pressure the explosions and after-effects are still more violent though the range of mixtures is not appreciably wider than at 2 atmospheres.

Initial Temperature 50°C; Various Initial Pressures. The results of experiments at increased initial temperature and 1 and 2 atmospheres initial pressure were not conclusive, for it is not possible to vary the initial temperature, keeping the pressure constant, without at the same time varying the initial density. Mean flame speeds are not appreciably altered by rise in initial temperature. The range of mixtures giving an audible explosion at 2 atmospheres initial pressure is slightly widened, but the violence of the after-effects is less than in similar mixtures at 15°C and 2 atmospheres pressure, probably owing to the decreased initial density. In no instance has a maintained shock wave been observed.

It appears, therefore, from these results on the effects of increased initial compression on the explosion of pentane-air mixtures, that effects can be obtained in a closed cylinder which would produce the manifestations of a pinking explosion in an engine cylinder. It has been established that the results are not due to changes in the initial mixture due to compression in the pump (preliminary oxidation); to impurities in the original pentane (such as high-boiling "nuclei"); or to any sudden molecular disruption giving rise to carbon or other abnormal end products. A trace of smoke is always observed in the products of the pinking explosions, but the amount of carbon so lost is not enough to appear in analyses when a "carbon balance" is drawn up. Such carbon particles may, however, be responsible for the highly luminous streaks which frequently appear in photographs of the glowing products of combustion.

Explosions of Mixtures of Benzene and Air

For comparison with the pinking explosions of pentane and air the behavior of a relatively nonpinking fuel, benzene, has been studied.

The mixture of benzene and air which on explosion under these conditions gives the greatest and most rapid development of pressure contains about 3 per cent of benzene by volume (10 to 1 air-benzene by weight). Pentane and benzene will, therefore, give the same maximum power mixture (vapor volumes) in an engine, though slightly less liquid benzene will be



FIG. 3. Benzene 2.8 per cent.
2 atm., 15°C. Nonpinking

required in view of its greater density. The magnitudes and mean rates of pressure development and the flame speeds are, throughout the inflammable range, somewhat higher with benzene than with corresponding pentane-air mixtures.

For mixtures of benzene and air at 1 atmosphere initial pressure and 30°C the explosions are throughout inaudible. This higher temperature has been chosen owing to the lower volatility of benzene. The afterburning is more diffused and continued than with pentane and commences more immediately in the wake of the flame (Fig. 3). At 2 atmospheres and 30°C the differences from pentane are marked. The afterburning proceeds regularly behind the initial flame and, though the range of mixtures containing from 3.2 to 3.8 per cent benzene by volume gives flame vibrations and a faintly audible explosion, there is no big pressure increment at the moment of extinction of the flame. In no instance has a shock wave been recorded. It appears that combustion, initiated in the flame front, proceeds continuously so that there is not sufficient energy available to maintain a shock wave when the rapidly vibrating flame strikes the far end plate.

Explosion of Blended Mixtures of Pentane and Benzene

In order to test this suggestion further experiments have been carried out on blends of pentane and benzene.

Mixtures containing pentane and benzene in approximate proportions 1 to 3, 1 to 1, 3 to 1, pentane to benzene by volume were made up to contain in each case about 3.5 per cent of inflammable vapor. These mixtures were ignited at 2 atmospheres initial pressure and 30°C. The flame photographs and pressure records show a gradual transition from the typical benzene explosion, in which the combustion is continuous behind the flame front, to that of pentane in which the afterburning is delayed until the flame strikes the end of the cylinder.

The most interesting observation is that, particularly in mixtures containing the inflammable constituents in equal proportions, ignition of the unburnt charge sometimes occurs ahead of the advancing flame. This most frequently happens after the "skirt," but before the center portion, of the flame reaches the end plate, but it has been known to take place before any portion of the flame has struck the end of the cylinder. These ignitions ahead of the initial flame, which invariably occur on or very near the end plate, give rise to a second flame which travels back to meet the initial flame at about the same speed. The explosions in these instances are not louder than usual and the pressure records show no unusual features. It would appear, therefore, that such an ignition of unburnt residual mixture is not likely to be the cause of a pinking explosion in an engine cylinder.

Explosion of Mixtures of Ethyl Ether and Pentane with Air

Further to test the suggestion that pinking is the outcome of energy release in the end products of the initial flame, rather than in the unburnt residue ahead of that flame, the effect of adding a "pro-knock" to the pentane-air mixtures has been investigated. The only nonexplosive compound which was known definitely to act in this way was ethyl ether. The H. U. C. of a straight-run No. 1 petrol in a variable-compression engine was lowered 0.26 per cent by addition of 10 per cent ethyl ether by liquid volume.

Isopentane containing 10 per cent liquid volume of ethyl ether was vaporized and diluted with air to give mixtures containing 3.5 per cent by volume of the composite vapor. The explosion of such mixtures in the closed cylinder at 30°C and 2 atmospheres initial pressure is violent. The flame photographs show little or no afterburning until the vibrating flame strikes the far end plate and there is a considerable pressure release at this point. In one instance there was an ignition of unburnt residue at the end plate ahead of the initial flame, but this did not in any

way affect the subsequent afterburning or the violence of the pink.

Additional support to the suggested explanation of the mode of combustion in pinking explosions has been gained from experiments in which the conditions were varied in an attempt to suppress pinking by such means as are found to be effective in an engine cylinder.

Suppression of Pinking

Reduction in Length of Cylinder.—By the use of the bucket-shaped end plate to which reference has previously been made, the length of the explosion cylinder was reduced to 10 inches (25.4 cm). With this length of cylinder, the initial pressure of a 3.5 per cent pentane-air mixture, initially at 15°C, has to be increased to 2.5 atmospheres before its explosion produces any sound or the photograph of the flame shows any of the characteristics of pinking. When the length of the cylinder is 15 inches (38.1 cm) this mixture gives an audible explosion at 1 atmosphere initial pressure. It seems that, at a given initial temperature and pressure, a certain minimum run is required before flame vibration is set up. Such flame vibration, leading to, or accompanied by flame acceleration, is the necessary forerunner of the shock which produces the sudden pressure release in a pinking explosion.

These observations are in accord with the well-known fact that the degree of pinking in an engine is very sensitive to variations in the distance between the spark plug and the most distant point in the combustion space.



FIG. 4. Pentane 3.4 per cent. Fan 1500 rpm. 2 atm., 15°C. Nonpinking

Turbulence. The evidence on the effect of turbulence of charge on pinking in an engine is somewhat confusing. It is well known that an engine pinks most readily when running slowly under a heavy load ("laboring"), but the possible effect of decreased speed in reducing throttling in the valves, thereby raising the volumetric efficiency, and hence the initial density of the charge, must not be overlooked. Too great a degree of turbulence is said to increase knocking, but this is probably a phenomenon more similar in effect to pre-ignition; namely, the explosion is so rapid that maximum pressure is reached before top dead center and the ignition range supplied for the magneto is not sufficiently flexible to overcome the trouble.

The turbulence induced by a rotating two-bladed fan in the closed cylinder has a great effect on the nature of the combustion of gaseous mixtures therein. At 2 atmospheres initial pressure and 15°C no mixture of pentane and air gave an audible explosion when the fan was rotated at 2500 rpm at a point about midway in the cylinder (Fig. 4). The rate of pressure development was greatly enhanced, but the records were in all cases perfectly smooth. A glow runs back throughout the cylinder at about the moment when the initial flame, which travels at nearly uniform speed, reaches the end plate. The combustion in the initial flame must be more complete in the turbulent mixtures, however, so that there is not sufficient energy available to maintain a shock wave.

Antiknock Compounds. Lead tetraethyl was selected as being the most effective of these



FIG. 5. Pentane 3.8 per cent, with lead tetraethyl vapor. 2 atm., 15°C. Pinking.

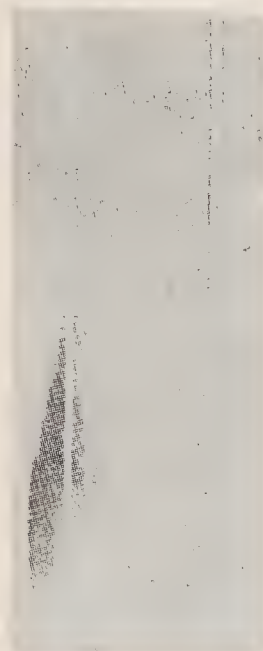


FIG. 6. Pentane 3.8 per cent, with lead tetraethyl decomposed. 2 atm., 15°C. Nonpinking.

substances. The addition of this compound to pentane, in amount corresponding to 2.5 fluid ounces per gallon (16.2 ml per liter) of pentane, greatly increases the violence of the explosion of a 3.5 per cent pentane-air mixture when ignited at 2 atmospheres and 15°C. The explosion is accelerated and the aftereffects are much more pronounced than with the undoped mixture (Fig. 5). When, however, the lead tetraethyl vapor is decomposed before igniting the mixture, the explosion is quite silent. The method has been to heat the lead tetraethyl in a glass bulb at about 300°C until a puff of smoke appears. This smoke is then allowed to pass into the cylinder with the entering pentane-air mixture. When such a large amount of dope is used [2.5 fluid ounces per gallon (16.2 ml per liter) of fuel], the flame photograph resembles that of a very rich pentane- or benzene-air mixture. There is no well-defined flame front, but combustion appears to be continuous (Fig. 6). In other experiments, the addition of very small amounts of lead tetraethyl has eliminated the shock wave and tended to produce a continuous combustion in the wake of the initial flame.

These results confirm the view of Egerton and Gates³ that it is the decomposition products of lead tetraethyl, and not lead tetraethyl itself, which have an antiknock action.

Shape of Combustion Space. Parallel experiments have been carried out on the explosion of mixtures of pentane and air in cubical and spherical vessels. In a cube or a sphere with central ignition no mixture at 1 atmosphere initial pressure

produces an audible explosion. When the initial pressure is 2 atmospheres there is a slight sound on explosion of a 3.5 per cent pentane-air mixture in a cube. The pressure record shows slight vibrations, but either the flame is not sufficiently rapid or the initial combustion more complete, because in no instance is there any indication of a shock wave. These results are in accord with the prevalent view that pinking in an engine, for a given compression ratio, is greatly reduced by having central ignition in a compact combustion-head.

Comparison of Pinking and Nonpinking Explosions

A study of the records on which this paper is based reveals the following differences between a pinking and a nonpinking explosion:

In a pinking explosion, such as those of pentane-air mixtures at high initial pressures, combustion is not completed in the flame front and is not continuous behind the flame. It would seem as though some additional impetus were

required to cause the completion of the reactions. When this impetus is given—for example, by the production of a shock wave when the accelerating, vibrating flame is arrested at the end of the cylinder—the combustion is completed almost instantaneously throughout the cylinder, with a consequent increase in pressure. This subsequent energy release may maintain the shock wave, thereby producing effects similar to those of a “detonation wave.”

In a nonpinking explosion, such as those of benzene-air mixtures, the combustion reactions are continuous and long-continued behind the flame front. Even when conditions are such that the initial flame can commence to vibrate and accelerate, its subsequent arrest does not lead to any violent aftereffects as the energy available is not sufficient.

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IMPORTANCE OF MIXTURE RATIO IN RATING FUELS FOR KNOCK

JOHN M. CAMPBELL, WHEELER G. LOVELL, AND T. A. BOYD

Research Laboratories, General Motors Corporation, Detroit, Michigan

It is shown that the knock rating of one fuel with respect to another may depend upon the carburetor setting at which the comparison is made. The influence of mixture strength is often so large that, unless careful attention is given to this factor during knock measurements, it is possible to obtain widely discordant results in spite of what may otherwise be the best of experimental technic.

If knock ratings of some fuels made by different laboratories are to be comparable, the different experimenters must agree upon some general specification as to the mixture ratio at which the measurements shall be made. Because it is both the point of highest intensity and one that can be located readily, it is proposed that knock measurements be made independently for each fuel at the mixture ratio giving its maximum degree of knock.

The tendency of a motor fuel to knock is influenced by several factors. Most of these may be classified under two general headings:

(a) Physical: Compression ratio, timing of the spark, speed of the engine, setting of the throttle, shape of the combustion chamber, timing of the valves, efficiency of cooling temperature of jacket water, and atmospheric conditions.

(b) Chemical: Composition of the fuel and mixture ratio.

In knock-testing one customary procedure is to make comparative measurements between some standard fuel and the fuel under test. The relative tendency to knock is then expressed in terms of some one of the preceding variables which affect the tendency to knock. Since there is a choice of variables, it is not surprising that several methods for making comparative measurements of knock have been proposed. But at the present time there does not appear to be satisfactory agreement between the results obtained by various laboratories using different methods for testing the same fuels.^{1,2} The purpose of this paper is to point out the importance of controlling mixture ratio during knock measurements, and to show that unless proper attention is given to mixture ratio it is possible to obtain widely discordant results in spite of what may otherwise be the best of experimental technic.

Experimental

This work was carried out upon a single-cylinder, variable-compression engine equipped with an evaporative cooling system and fitted with a bouncing-pin indicator. The compression ratio was adjusted to give a fairly loud knock with the fuel under examination. The speed was held at 850 rpm and the spark advance was set at 30 degrees. The fuel was metered to the engine through a mixing valve. The mixture ratio was

adjusted by changing the fuel level with respect to the fuel jet in the mixing valve. Figure 1 shows the fuel reservoirs, the two float bowls independently adjustable for height by means of a rack and pinion, and the three-way cock for changing

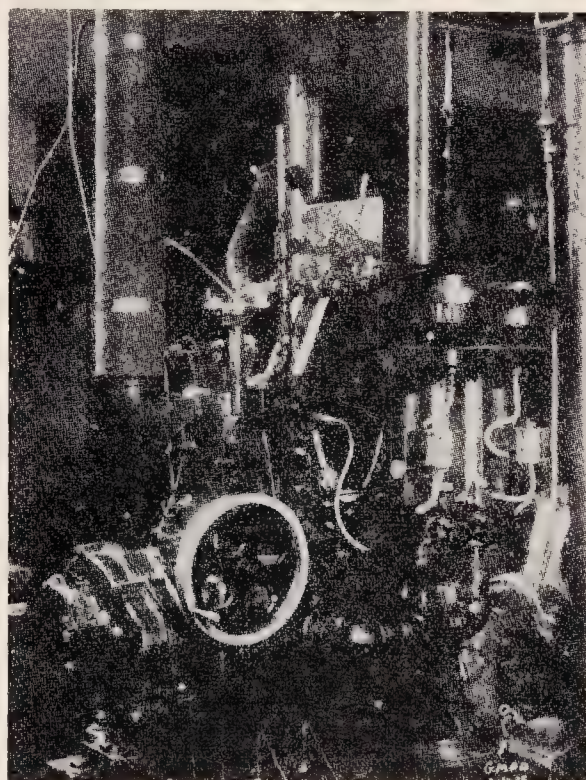


FIG. 1. Variable compression engine equipped with bouncing-pin indicator, mixing valve, and adjustable float bowls for controlling mixture ratio.

from one fuel to another. The mixing valve is shown also.

Before beginning each run, the engine was allowed a preliminary warming-up period, and during this time bouncing-pin measurements were taken on one of the test fuels. When the constancy of these readings was enough to assure

uniform results for some time to come, the run was started. Bouncing-pin readings were taken successively for each fuel at each fuel level. This cycle was repeated three times. Samples of exhaust gas were taken at each fuel level while the engine was running on gasoline containing ethyl fluid. Determination of carbon dioxide in these samples served as a key to the mixture ratio at each fuel level.

The *n*-heptane, the isooctane (2,2,4-trimethylpentane), and the ethyl fluid used in this work were obtained from the Ethyl Gasoline Corporation. The ethyl fluid contained 54.5 per cent by volume of lead tetraethyl. The gasoline used as a standard in these experiments was a widely used automobile gasoline.

Physical properties of materials

Material	Source	<i>d</i> (20°/4°C)	Boiling point, °C
<i>n</i> -Heptane	Jeffrey pine	0.6859	96.8–99.4
Isooctane	oil synthesis	0.6911	97.6–99.8
Benzene, c.p.		0.8775	78.6–79.6

Results

The results of several runs are presented in Tables I to V. From these data Figs. 2 to 8 were constructed. The mixture ratios were determined

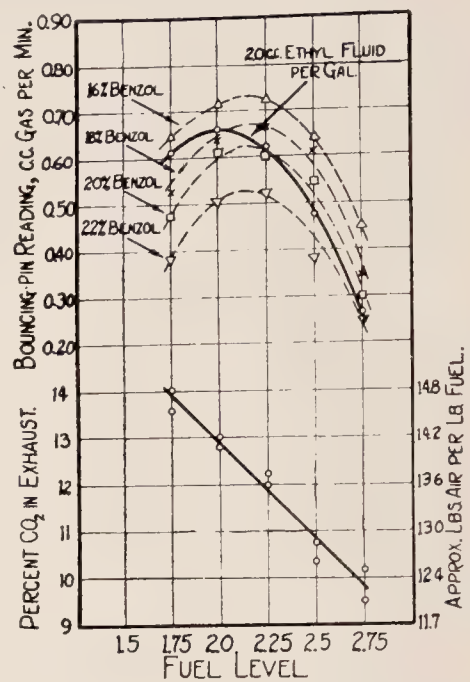


FIG. 2. Comparison of benzol blends with gasoline containing 2.0 cc of ethyl fluid per gallon.

in terms of conventional units as pounds of air per pound (1 pound = 0.454 kg.) of fuel corresponding to the different fuel levels by referring the percentage of carbon dioxide in the exhaust gases at each fuel level to a representative plot of

TABLE I

Comparison of benzene blends with gasoline containing 2.0 cc of ethyl fluid per gallon (3.78 liters)

		Bouncing-pin readings, cc gas per minute				
Fuel level	CO ₂ in exhaust gasoline	2.0 cc ethyl fluid per gal.	Benzene in gasoline			
			16%	18%	20%	22%
Inches	Per cent	cc	cc	cc	cc	cc
2.00	13.0	0.64	0.72	0.62	0.62	0.50
2.25	12.0	0.66	0.68	0.68	0.61	0.49
2.50	10.8	0.45	0.62	0.60	0.50	0.44
3.00	10.2	0.26	0.43	0.30	0.26	0.21
1.75	13.6	0.57	0.63	0.50	0.43	0.32
2.00		0.69	0.71	0.65	0.60	0.50
2.25		0.61	0.75	0.65	0.61	0.50
2.50		0.47	0.64	0.59	0.55	0.50
3.00		0.25	0.44	0.38	0.35	0.30
1.75		0.63	0.63	0.51	0.55	0.44
2.00	12.9	0.65	0.70	0.64	0.61	0.48
2.25	12.2	0.60	0.73	0.69	0.61	0.52
2.50	10.4	0.50	0.70	0.64	0.60	0.50
3.00	9.6	0.31	0.51	0.35	0.30	0.30
1.75	14.0	0.64	0.63	0.53	0.50	0.41

TABLE II

Comparison of benzene blends with gasoline containing 5.0 cc of ethyl fluid per gallon

Bouncing-pin readings, cc gas per minute						
Fuel level	CO ₂ in exhaust gasoline	5.0 cc ethyl fluid per gal.	Benzene in gasoline			
			30%	33%	35%	37%
Inches	Per cent	cc	cc	cc	cc	cc
3.00	9.3	0.26	0.60	0.51	0.41	0.31
2.50	10.4	0.49		0.71	0.68	0.49
2.25	11.6	0.48		0.75	0.69	0.52
2.00	12.8	0.63		0.79	0.75	0.60
1.75	13.2	0.69	0.82	0.68	0.59	0.45
1.50	14.0	0.62	0.68	0.48	0.36	0.28
1.75		0.69	0.80	0.60	0.52	0.40
2.00		0.62		0.80	0.68	0.59
2.25		0.50		0.78	0.68	0.51
2.50		0.42		0.65	0.60	0.42
3.00		0.27	0.70	0.47	0.40	0.31
1.50		0.61	0.52	0.43	0.41	0.29
1.75	13.8	0.71	0.73	0.64	0.60	0.49
2.0	12.4	0.64		0.81	0.65	0.60
2.25	11.4	0.52		0.78	0.68	0.58
2.50	10.8	0.43		0.72	0.60	0.50
3.00	9.4	0.25		0.53	0.40	0.35
1.50		0.60		0.40	0.39	0.30

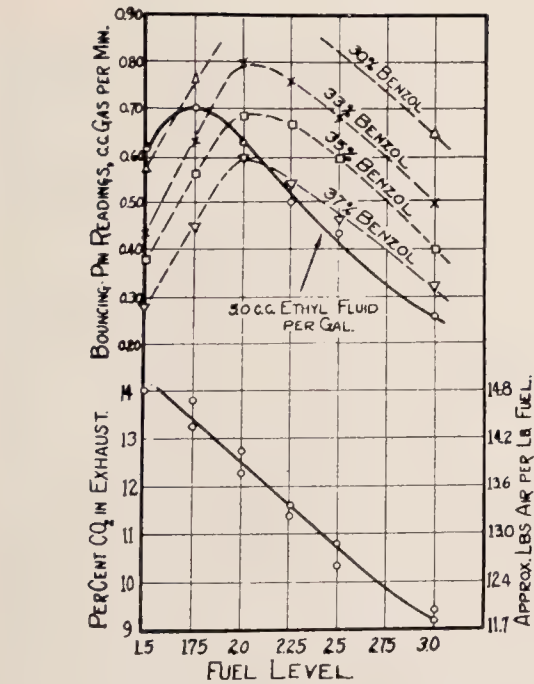


FIG. 3. Comparison of benzol blends with gasoline containing 5.0 cc of ethyl fluid per gallon.

exhaust gas composition against mixture ratio. These values for mixture ratio do not apply to the benzene blends nor to mixtures of heptane and octane which have physical and chemical properties that are different from those of gasoline. In plotting the readings of the bouncing-pin indicator the average of the readings for each fuel at each fuel level was plotted instead of the individual values, in order that the charts might be read as easily as possible.

A study of the figures indicates that the rating of one fuel with respect to another depends upon the carburetor setting at which the determination was made. For example, in Fig. 2 at the carburetor adjustment corresponding to a mixture ratio of 14.8 pounds of air per pound of gasoline, 17 per cent benzene in the standard gasoline appears to be equivalent to 2.0 cc of ethyl fluid per gallon in the same standard gasoline, whereas at the carburetor adjustment corresponding to an air-gasoline mixture ratio of 12:1, it would take 22 per cent of benzene to be equivalent to the same amount of ethyl fluid. Likewise, the data plotted in Fig. 3 show that 5.0 cc of ethyl fluid per

TABLE III

Comparison of fuel containing 48 per cent *n*-heptane and 52 per cent isooctane with gasoline alone and with gasoline containing 0.5 cc of ethyl fluid per gallon

Bouncing-pin readings, cc gas per minute				
Fuel level	CO ₂ in exhaust gasoline	Standard gasoline	0.5 cc ethyl fluid per gal. gasoline	48% <i>n</i> -heptane 52% isooctane
Inches	Per cent	cc	cc	cc
1.75	13.2	0.48	0.30	0.35
2.00		0.48	0.41	0.58
2.25		0.72	0.59	0.69
2.50		0.68	0.60	0.70
2.75		0.55	0.49	0.60
3.0	9.7	0.48	0.31	0.46
3.25	13.4	0.39	0.25	0.35
1.75		0.51	0.40	0.36
2.00		0.72	0.56	0.65
2.25		0.72	0.62	0.75
2.50		0.74	0.54	0.71
2.75		0.60	0.45	0.62
3.00		0.51	0.26	0.48
3.25		0.52	0.20	0.39
1.75		0.50	0.31	0.47
2.00		0.74	0.60	0.65
2.25		0.80	0.66	0.76
2.50		0.75	0.65	0.70
2.75		0.68	0.50	0.61
3.00		0.51	0.33	0.50
3.25		0.37	0.26	0.38

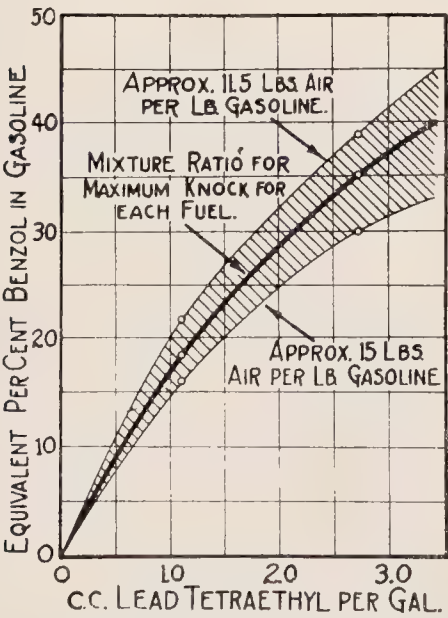


FIG. 4. How mixture ratio affects relationship between antiknock properties of benzol and lead tetraethyl.

gallon in the standard gasoline may be determined as equivalent to concentrations of from 30 to 39 per cent benzene in the standard gasoline, according to the carburetor adjustment, when the latter is the same for both fuels. There is, therefore, a considerable range in composition of benzene blends which appear to have a tendency to knock equivalent to a given concentration of lead tetraethyl in gasoline. This range is indicated by the shaded portion of Fig. 4. The shaded area on the chart may be used also to interpret the range of lead tetraethyl equivalent to a given benzene blend. Thus, it shows that from 1.3 to 2.0 cc of lead tetraethyl per gallon may be found equivalent to 25 per cent benzene in gasoline, the value found depending upon the carburetor setting at the time the determination was made.

The last three runs using mixtures of *n*-heptane and isooctane as the standard fuel show a similar effect, although the range of composition having equivalent ratings against lead tetraethyl at different mixture ratios is not so wide as for benzene. Figure 8 is a plot of heptane-octane

TABLE IV

Comparison of fuel containing 38 per cent *n*-heptane and 62 per cent isooctane with gasoline containing 1.5 and 2.0 cc of ethyl fluid per gallon, respectively

Fuel level	CO ₂ in exhaust gasoline	Bouncing-pin readings, cc gas per minute		
		Ethyl fluid in gasoline		38% <i>n</i> -heptane 62% isooctane
		1.5 cc/gal.	2.0 cc/gal.	
Inches	Per cent	cc	cc	cc
1.75		0.23	0.19	0.11
2.00	13.8	0.38	0.30	0.27
2.25		0.58	0.41	0.37
2.50	11.6	0.50	0.39	0.38
2.75		0.49	0.30	0.31
3.00	9.6	0.33	0.21	0.25
1.75		0.28	0.25	0.17
2.00		0.41	0.39	0.28
2.25		0.51	0.41	0.44
2.50		0.58	0.36	0.46
2.75		0.39	0.32	0.39
3.00		0.32	0.24	0.32
1.75		0.31	0.24	0.15
2.00		0.46	0.38	0.26
2.25		0.58	0.45	0.41
2.50		0.55	0.36	0.41
2.75		0.41	0.30	0.35
3.00		0.31	0.24	0.28

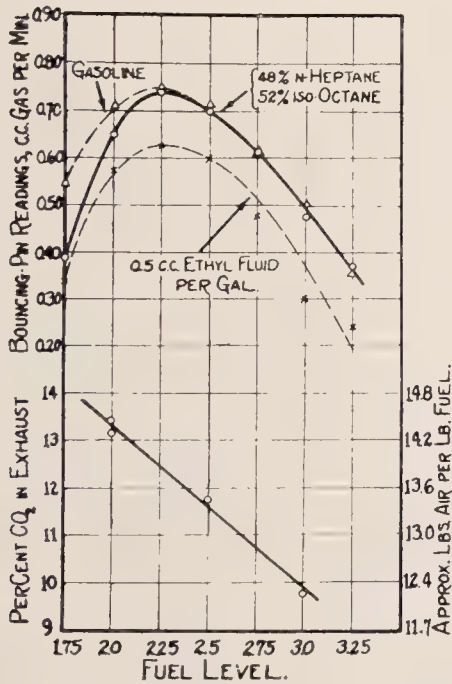


FIG. 5. Comparison of fuel containing 48 per cent *n*-heptane and 52 per cent isooctane with gasoline alone and with gasoline containing 0.5 cc ethyl fluid per gallon.

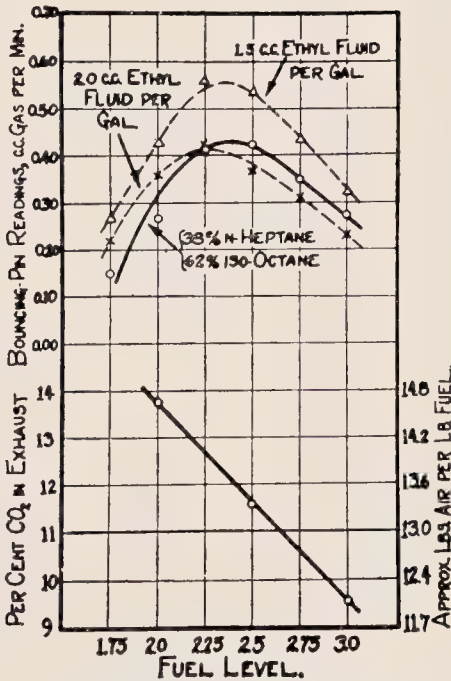


FIG. 6. Comparison of fuel containing 38 per cent *n*-heptane and 62 per cent isooctane with gasolines containing 1.5 and 2.0 cc of ethyl fluid per gallon, respectively.

TABLE V

Comparison of fuel containing 27 per cent *n*-heptane and 73 per cent isooctane with gasolines containing 4.5 and 5.0 cc of ethyl fluid per gallon, respectively

Fuel level	CO ₂ in exhaust gasoline	Bouncing-pin readings, cc gas per minute		
		Ethyl fluid in gasoline		27% <i>n</i> -heptane 73% isooctane
		4.5 cc/gal.	5.0 cc/gal.	
Inches	Per cent	cc	cc	cc
2.50	12.9	0.53	0.45	0.50
2.75		0.49	0.37	0.44
3.00		0.35	0.18	0.24
2.25	13.0	0.54	0.47	0.49
2.00		0.48	0.39	0.40
2.00	13.8	0.48	0.45	0.40
2.25		0.54	0.45	0.45
2.50		0.48	0.40	0.50
2.75	12.0	0.40	0.32	0.48
3.00		0.20	0.28	0.31
3.25		0.20	0.19	0.22
3.50	9.6	0.10	0.08	0.08
3.25		0.12	0.13	0.27
3.00		0.31	0.30	0.44
2.75		0.41	0.39	0.48
2.50	12.2	0.51	0.40	0.52
2.25		0.51	0.41	0.50
2.00		0.48	0.31	0.38
3.25		0.17	0.14	0.17

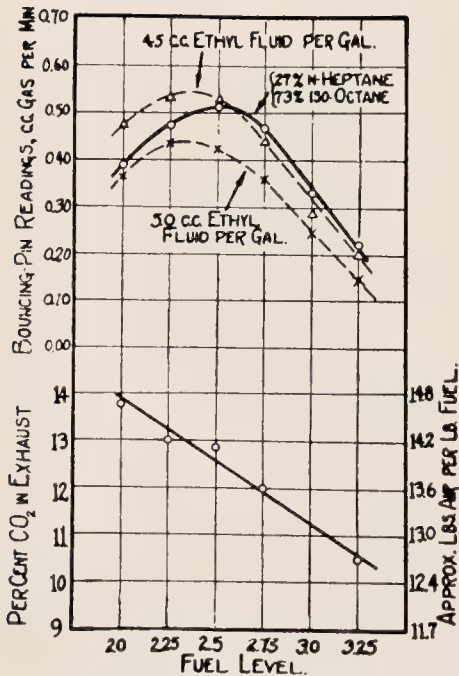


Fig. 7. Comparison of fuel containing 27 per cent *n*-heptane and 73 per cent isooctane with gasolines containing 4.5 and 5.0 cc of ethyl fluid per gallon, respectively.

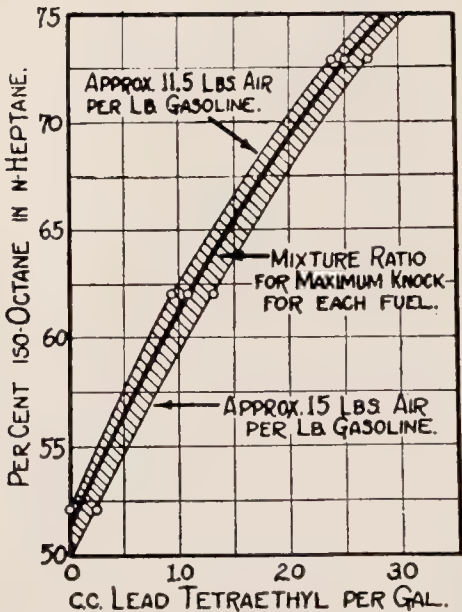


Fig. 8. How mixture ratio affects relationship between antiknock properties of *n*-heptane-isooctane mixtures, and lead tetraethyl.

composition against lead tetraethyl in the standard gasoline, at mixture ratios between 11.5:1 and 15:1 for gasoline.

Discussion

One fundamental assumption in almost every method for measuring knock has been that changes in the variables which influence knock have the same effect upon all fuels. This assumption is decidedly erroneous when applied to changes in mixture ratio. It is possible to have two fuels, *A* and *B*, of different composition which knock just alike at one carburetor adjustment, although at a leaner adjustment *A* may knock less than *B* and at a richer adjustment *A* may knock more than *B*. As an illustration, consider 18 per cent benzene and 2.0 cc of ethyl fluid per gallon in Fig. 2 as fuels *A* and *B*, respectively. At the carburetor setting corresponding to about 13.8 pounds of air per pound of gasoline these two fuels knock alike, but at leaner mixture ratios 18 per cent benzene knocks less and, at richer mixture ratios, more than 2.0 cc of ethyl fluid per gallon. In other words, the rate of change in tendency to knock with respect to changes in carburetor adjustment varies according to the chemical composition of the fuel.

Therefore, in order that different laboratories may be able to obtain comparable and reproducible measurements of knock, it is necessary to decide upon some common mixture strength at which knock-testing shall be done. This mixture ratio must be adhered to closely because the tendency to knock is sensitive to comparatively small changes in mixture ratio.

The question arises—what mixture ratio shall be chosen? It seems hardly practicable to select a certain mixture ratio at random. This would

require the constant use of gas-analysis apparatus or some device for measuring both air and fuel in order to make sure that the mixture ratio was properly adjusted. The procedure would become quite complicated with fuels which have different products of combustion and different physical properties. The mixture ratio for maximum power would not be suitable because power measurements are not sufficiently sensitive to changes in mixture ratio to make a satisfactory adjustment possible.

There remains one outstanding and comparatively simple solution. For every fuel there is a definite mixture ratio at which maximum knock occurs; and, if the determinations are made at the mixture ratio for maximum knock with each individual fuel, there is available a standard for obtaining reproducible results by different laboratories.

Conclusions

1. The tendency of a fuel to knock is very sensitive to changes in mixture ratio.
2. Since the change in tendency to knock with changes in carburetor adjustment varies according to the composition of the fuel, it is necessary to choose some definite ratio mixture for knock-testing work if reproducible results are to be obtained.
3. The use of mixture ratios giving maximum knock for each fuel is suggested as a convenient means for obtaining more consistent results between different laboratories.

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1. EDGAR: J. Soc. Automotive Eng. 22, 41 (1928).
2. MACCOULL: *Ibid* 22, 457 (1928).

ACTION OF ACCELERATORS AND INHIBITORS UPON THE OXIDATION OF LIQUID HYDROCARBONS

T. E. LAYNG AND M. A. YOUKER

University of Illinois, Urbana, Illinois

An apparatus has been devised and a method described for determining the effect of various inhibitors and accelerators of knock upon the slow oxidation of hydrocarbon fuels. Data are given to show the effect of various substances upon the slow oxidation of *n*-heptane and its normal oxygen derivatives, gasoline, and kerosene. A surprising similarity is shown between the action of lead tetraethyl and various compounds of sodium and potassium, and also a difference in the action of lead tetraethyl and these compounds of sodium and potassium upon the oxidation of hydrocarbons, in the gas or liquid phases.

The status of the mechanism of oxidation of hydrocarbons, or the cause of detonation in the internal-combustion engine, is still in an unsatisfactory state. The use of antiknock substances, notably lead tetraethyl, has added a new factor and has been the cause of increasing vastly the amount of useful information which must be obtained for the solution of this problem.

In a recent summation of our knowledge of this subject Clark¹ shows that at the present time no theory is without its defects, but the peroxide theory supported by the work of Moureu, Dufraisse, and Chaux,² Callendar,³ and more recently of Mardles,⁴ appears the most promising. This theory postulates that detonation at high compression is due to the formation of explosive peroxides by the oxidation of liquid droplets of the fuel. The above investigators and also Lewis⁵ studied the action of oxygen upon various hydrocarbon fuels in the presence of catalysts at different temperatures. This method of study has also been advocated by Clark.⁶

The present investigation was undertaken in the hope of designing a more efficient apparatus and thus producing a means of securing more data in regard to the action of catalyst of oxidation and the causes of detonation. The results of preliminary work are presented herein.

Apparatus

The experiments on which Moureu and his associates based their conclusions were conducted with the fuel to be tested and the oxygen in a small glass bulb with a manometer attached. When the bulb was immersed in a hot bath, the rise of mercury in the manometer was a measure of the oxygen absorption and hence also of the rate of peroxide formation. Lead tetraethyl and other antiknock substances, such as the aromatic amines, retarded the absorption of oxygen. Peroxides were detected in the final products when oxygen had been absorbed.

The method of recording pressures in the apparatus of Lewis and Mardles was similar to

that employed by Moureu. In each case it was possible for some of the fuel to be distilled and condensed in the manometer connections.

Accordingly, an apparatus (Fig. 1) was designed which was extremely simple and eliminated any possibility of distillation. The Pyrex bulb is of an average volume of 160 cc. The side arm permits easy cleaning, the introduction of solid catalysts, and the withdrawal of

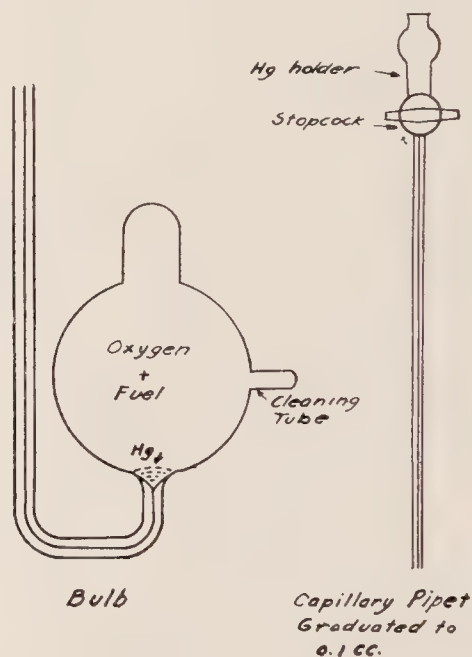


FIG. 1. Apparatus.

gas samples. The mercury in the base seals off the bulb and gives a column of mercury when the bulb is heated which enables changes in the pressure of the enclosed system to be detected. Since the entire bulb is immersed, changes in pressure under constant-temperature conditions can only be caused by the thermal decomposition of the fuel or its chemical union with oxygen.

In this apparatus there has been introduced the added factor of mercury in contact with the fuel when in the liquid phase, and with the fuel and

oxygen in the case of the gaseous phase. However, no mercury compounds have been shown to have any effect upon the rate of oxidation, and since in all the tests with different accelerators and inhibitors a comparison is made with the fuel alone, any effect of the mercury may be assumed a constant for a given fuel at a given temperature.

Before using, the bulb was cleaned in hot sodium hydroxide solution, washed out with dilute hydrochloric acid, and rinsed several times in distilled water. It was then washed out twice with acetone and dried. It was found to be very important to clean the bulbs very carefully.

The side arm was sealed off and after evacuation the bulb was filled with dry oxygen.

The fuel to be introduced was drawn up to the desired amount in the capillary pipet shown in Fig. 1, and held there by closing the stopcock. Mercury was then run into the bulb above the stopcock. The capillary tube of the apparatus was then connected to the tip of the pipet with a short piece of carefully cleaned rubber tubing, and on opening the stopcock the mercury forced the material into the bulb.

A sufficiently long piece of soft-glass capillary tubing was then connected to the capillary on the bulb by a short piece of heavy tubing, the bulb immersed in a well-stirred oil bath maintained at the desired temperature, and the pressure in the bulb noted by the height of the mercury column.

Preliminary Experiments

Some preliminary experiments, shown graphically in Fig. 2, were made to determine the type of data which might be obtained.

Some 0.5-cc samples of a pressure-still gasoline and various fractions thereof were subjected to oxygen for 8 hours at 160°C. No absorption of oxygen was noted, but rather a small increase in pressure.

Other 0.5-cc samples of the same gasoline connected with a manometer of the Moureu type showed a large absorption under the same temperature conditions. It was noted also that if the bulb was not completely immersed in the bath a brown gum formed in the bulb at the surface of the bath.

While this apparatus differs from that of Moureu, especially in size, and was not to be expected to yield the same data, nevertheless these experiments indicated that variable data may be obtained if any part of the fuel was not subjected to the desired temperature.

Benzaldehyde gave a rapid and smooth absorption at 160°C. Parawax showed a preliminary absorption followed by an increase in pressure

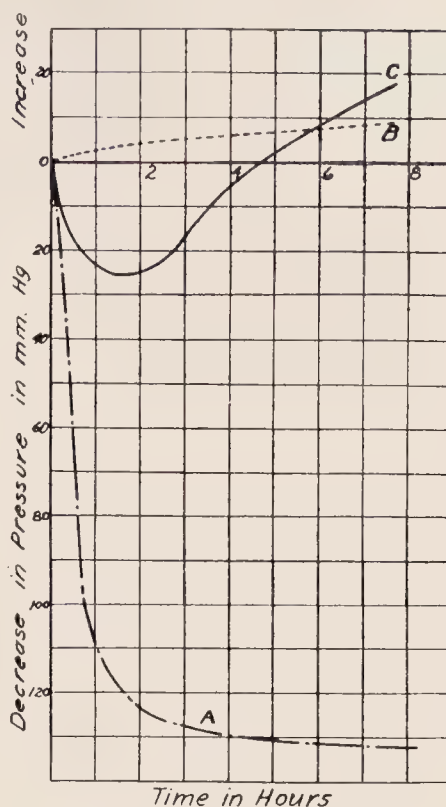


FIG. 2. Oxidation of: A—Gasoline in bulk with outside manometer; B—Gasoline in new apparatus; C—Parawax in new apparatus. All at 160°C.

at 160°C. Raising the temperature increased the amount of absorption.

Evidences of oxidation were noted in the degree of browning and gumming, in the increase in pressure, and in the amount of carbon dioxide found in the bulbs.

Experiments with *n*-Heptane and Its Normal Oxygen Derivatives

The mechanism of the oxidation of a hydrocarbon of the methane series is best expressed by the hydroxylation theory or by successive oxidation, forming the alcohol, the aldehyde, and the acid. Accordingly it was decided to determine the type of data which might be obtained on the slow oxidation of *n*-heptane, heptyl alcohol, heptaldehyde, and heptoic acid, when subjected to different accelerators and inhibitors at 160°C (Figs. 3 and 4).

n-Heptane. The pure compound is oxidized to a dark brown color in 20 hours. This oxidation was also indicated by a pressure rise of 40 to 50 mm.

Inhibition or prevention of this oxidation may be obtained by 1 per cent of ethyl fluid (containing 50 to 60 per cent of lead tetraethyl), potassium lactate, potassium tartrate, potassium heptylate, potassium diphenylamine, potassium ethylate,

aniline, diphenylamine, and sodium heptylate. No effect on the oxidation was produced by small amounts of calcium lactate, sodium tartrate, and *n*-tributylheptyl ammonium iodide. Acceleration of the oxidation was produced by 1 per cent of butyl nitrite.

Aldehydes and acids were detected in the product of the oxidation of the heptane, but none were found when the oxidation had been inhibited as by lead tetraethyl.

No positive tests for peroxides were obtained using potassium iodide and starch.

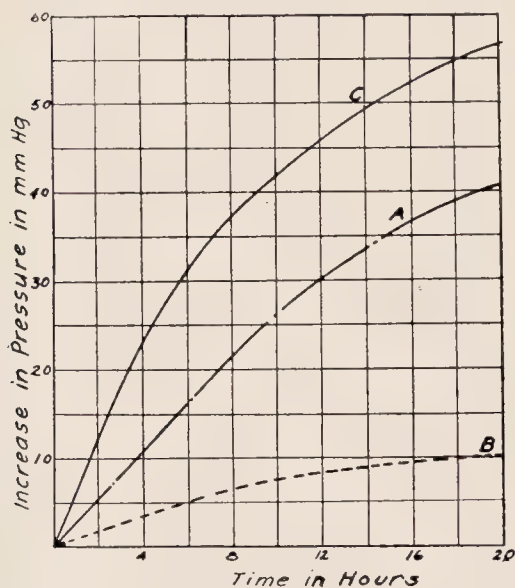


FIG. 3. Oxidation of: A—Pure *n*-heptane; B—*n*-Heptane plus 1% ethyl fluid; C—*n*-Heptane plus 1% butyl nitrite at 160°C.

n-Heptyl Alcohol. *n*-Heptyl alcohol showed no tendency to oxidize when pure and when containing 1 per cent of ethyl fluid by volume. When one per cent of butyl nitrite was added, a decrease in pressure was noted which was followed by a regular increase in pressure. If in addition to the butyl nitrite, 1 per cent of the ethyl fluid was added, this decrease in pressure was delayed about 4 hours, when a duplicate curve was obtained.

Heptaldehyde and Heptoic Acid. Oxidation progressed quite rapidly, as indicated in Fig. 4. One per cent of ethyl fluid had no marked effect. If anything, ethyl fluid appeared to accelerate the oxidation.

Two important results of this series are indicated. Heptane, heptaldehyde, and heptoic acid are progressively more easily oxidized. Heptyl alcohol is oxidized only with difficulty and *n*-heptane does not form the alcohol in its slow progressive oxidation.

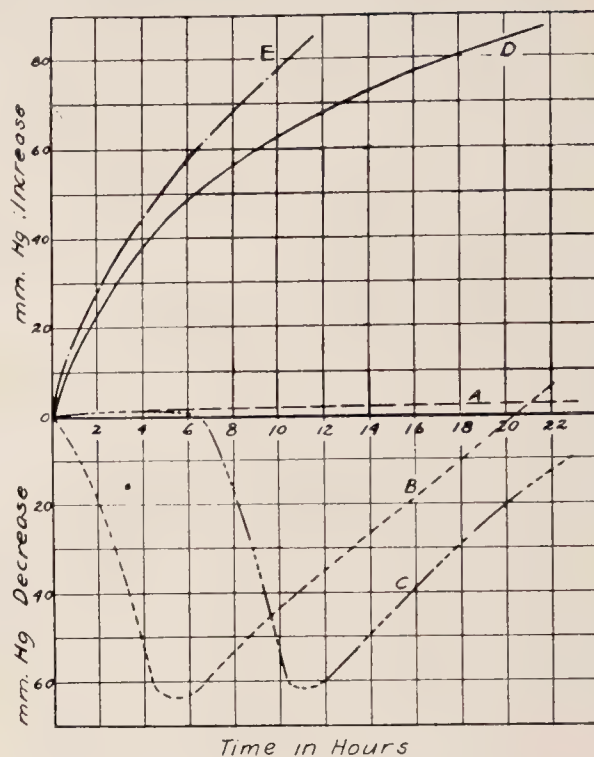


FIG. 4. Oxidation of: A—Heptyl alcohol; B—Heptyl alcohol plus 1% butyl nitrite; C—B plus 1% ethyl fluid; D—Heptaldehyde; E—Heptoic acid at 160°C.

Lead tetraethyl has the ability to delay the oxidation of heptyl alcohol when accelerated by butyl nitrite, but when started the path of oxidation is identical with that in which no delay occurs.

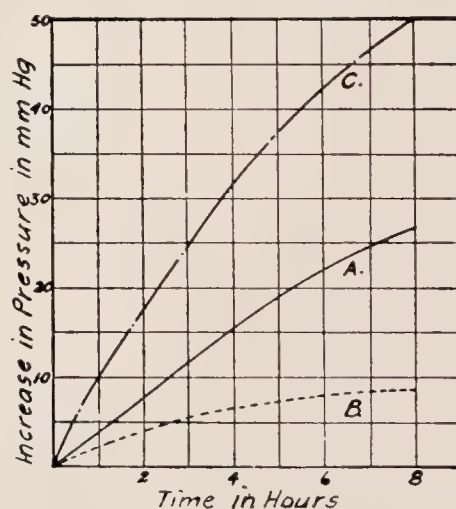


FIG. 5. Oxidation of: A—0.1 cc cracked gasoline, CO₂ = 8.5%, CO = 4.0%, Brown; B—A + 1% ethyl fluid, CO₂ = 5.1%, CO = 1.5%, Clear; C—A + 1% butyl nitrite, CO₂ = 13.1%, CO = 6.2%, Brown. All at 200°C for 8 hours.

Experiments with Gasoline

n-Heptane offers undoubtedly the best opportunities for obtaining definite data. On account of the small quantity that the writers were able to obtain, together with the difficulty of correlating any data obtained with those from gasoline and kerosene, it was decided to determine the inhibiting and accelerating effects of different substances upon gasolines.

Samples of pressure-still gasoline and its sulfonated and carefully washed residue were subjected to slow oxidation at 130°, 160°, and 200°C. Further samples containing 1 per cent of butyl nitrite or ethyl fluid were also tested at these temperatures in amounts from 0.1 to 1.0 cc.

No conclusive results were obtained with either the original or sulfonated samples at the two lower temperatures, except that butyl nitrite accelerated the oxidation as it did at the highest temperatures.

At 200°C the lead tetraethyl inhibited the oxidation (Fig. 5).

The most decisive indication of these experiments with gasoline, then, was that a temperature of 200°C must be used before definite results may be obtained. Since at 200°C practically all of the gasoline used was in the gas phase, for definite results the physical condition of the fuel was important.

As a result of these findings it was decided to attempt a correlation of this method of study of the mechanism of oxidation in the presence of inhibitors and accelerators with their recognized evaluation which had been obtained by actual engine tests. For this purpose a gasoline from the

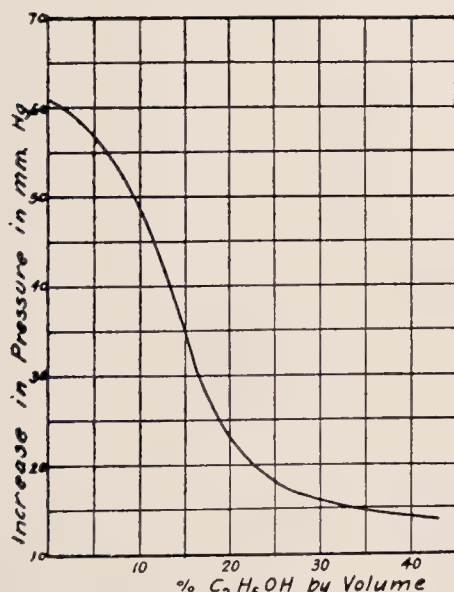


FIG. 6. Effect of C_2H_5OH on oxidation of Pennsylvania gasoline in vapor phase at 200°C.

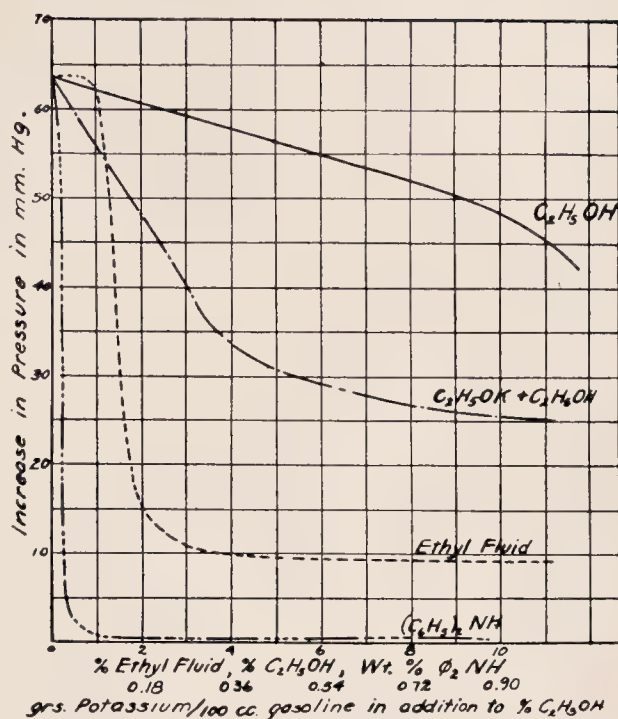


FIG. 7—Effect of $PbEt_4$, C_2H_5OH , C_2H_5OK , $(C_6H_5)_2NH$ on oxidation of Pennsylvania gasoline in vapor phase at 200°C.

straight-run distillation of Pennsylvania paraffin-base crude was obtained. By varying the temperature and the amount of gasoline, it was found that 0.2 cc oxidized fairly rapidly, giving a considerable increase in pressure in 6 hours.

For the comparison with engine-test evaluations of inhibitors, it was decided to use ethyl fluid and diphenylamine, and since the alkali-metal compounds in the first series of experiments gave promise of possessing inhibiting properties, potassium ethylate, ethyl alcohol, and potassium-substituted diphenylamine were also added to the list. The ethylate of potassium was chosen because it was easy to prepare, and with the addition of a little alcohol was sufficiently soluble in the gasoline. The results of these experiments are shown in Figs. 6 and 7.

One indeterminate factor in the choice of lead tetraethyl for these tests at this temperature is caused by its instability and explosive character when heated alone with oxygen. The writers were unable to determine the effect of this factor upon the pressure changes. The gasoline alone with oxygen showed an increase in pressure of about 60 mm. The bulbs were completely coated with a uniform brown deposit. Ethyl fluid was then added in increasing amounts. Up to 1 per cent it did not affect the oxidation, but when 2 per cent was added only a small pressure rise occurred. The bulbs and the gasoline remained undischored by the 7 hours of heating at 200°C.

Ten per cent or less of the ethyl fluid did not eliminate an increase in pressure of about 10 mm. The most noticeable effect of larger amounts of ethyl fluid was a small deposit on the bulbs due to the lead compounds present.

Diphenylamine in amounts of from 1 to 10 grams per 100 cc of gasoline inhibited the oxidation as well or better than the ethyl fluid. This is equivalent to almost one hundred times the engine rating of diphenylamine as compared with lead tetraethyl.

Potassium ethylate in amounts of from 0.09 gram to 1.44 grams of potassium per 100 cc gasoline was next tested. With 0.72 gram of potassium per 100 cc the brown discoloration was prevented, with 1.08 grams per 100 cc there was no apparent consumption of oxygen.

On account of the presence of small volumes of ethyl alcohol with the potassium ethylate, its effect on the oxidation of the gasoline was next determined. Little effect was noted up to 10 per cent by volume. From 20 to 40 per cent of the alcohol produced little change in the final pressure. The brown discoloration always accompanying oxidation faded rapidly in percentages above 20.

The substituted potassium compound of diphenylamine was next prepared. It was not soluble to any extent in gasoline unless some alcohol was added. This made it uncertain whether the potassium was in the amine or split off to form some ethylate. In any case the oxidation of the gasoline was completely stopped by a small percentage of the inhibitor.

Solid potassium thiocyanate and caesium dichloro-iodide gave somewhat doubtful results, possibly inhibiting slightly.

The results obtained in this series of experiments indicated that there was no relation between engine-test evaluations of inhibitors and their relative values when obtained by the slow oxidation of a badly knocking gasoline in the vapor phase. The data also showed that potassium ethylate and potassium-substituted diphenylamine possessed marked inhibiting properties in the vapor-phase oxidation of gasoline.

Oxidation of Kerosene

From the preceding series of experiments, it appeared that a careful study of the effect of inhibitors upon a hydrocarbon fuel in the liquid phase might lead to some important results. In fact, such data might show that engine-test evaluations of inhibitors were comparable only with oxidation in the liquid phase.

Accordingly, the effect of the inhibitors studied in the series of gas-phase oxidations was determined in this series of experiments in which the

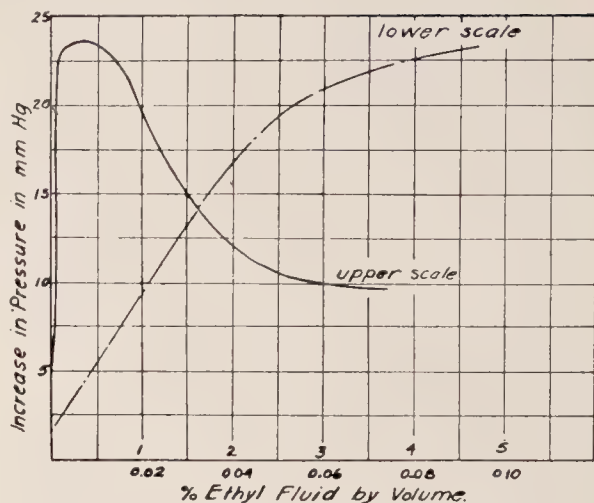


FIG. 8. Effect on catalysis of oxidation of kerosene by ethyl fluid—3 hours at 180°C.

fuel, kerosene, was almost wholly in the liquid phase. Kerosene was chosen, since the temperature at which the gasoline would be in the liquid phase would give too slow a rate of oxidation. The results are shown in Figs. 8 and 9.

It was found that 0.5 cc of kerosene could be heated for as long as 8 hours at 180°C without more than a slight oxidation. However, the addition of a small percentage of ethyl fluid caused a pronounced oxidation of the kerosene. An increase in the pressure was noted. The brown gummy product always indicative of oxidation was quite pronounced and, instead of coating the whole inner surface of the bulb as in the case of the gasoline, was found only where the liquid kerosene had been. On removing the bulb from the bath and connecting with a buret containing air, it was found that much of the oxygen present in the bulbs had been used in the oxidation process.

The accelerating action of the lead tetraethyl

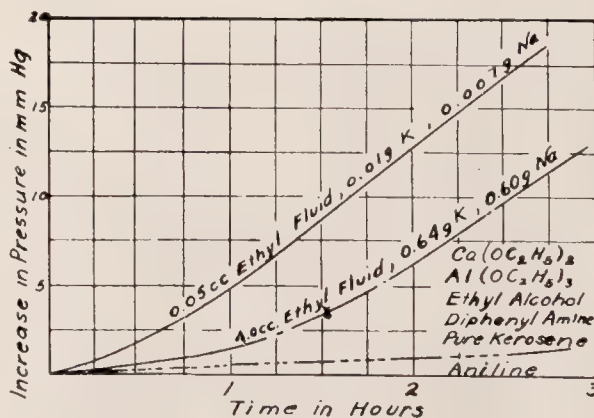


FIG. 9. Effect of KOC_2H_5 , NaOC_2H_5 , PbEt_4 , etc., on oxidation of a kerosene at 180°C. All amounts of catalysts are per 100 cc of kerosene.

reached a maximum when present in very small percentages. Increasing the percentage apparently decreased its effect on the rate of oxidation.

As little as 0.05 cc of ethyl fluid per 100 cc of kerosene (approximately 0.03 cc lead tetraethyl per cc) has a pronounced effect on the oxidation of the 0.5-cc kerosene sample at 180°C. About 0.3 cc of ethyl fluid per 100 cc of kerosene appeared to exert the maximum effect.

Aromatic amines were next tested. One gram of diphenylamine per 100 cc of kerosene had no action. Aniline in percentages of from 1 to 10 by volume had no action.

Alcohol in percentages of from 1 to 20 by volume had no action.

Potassium ethylate exhibited catalytic properties similar to those of lead tetraethyl. Its accelerating action reached a maximum when present in very small percentages. This percentage could be increased largely without changing materially the amount of oxidation. With 0.01 gram of potassium per 100 cc of kerosene the maximum oxidation of the kerosene took place. As little as 1 mg. of potassium per 100 cc appeared to be capable of causing the brown gummy deposit at the base of the bulb where the liquid was in place.

Sodium ethylate exhibited properties similar to those of potassium ethylate and of lead tetraethyl. 0.007 gram of sodium per 100 cc of kerosene appeared to produce the maximum amount of oxidation.

Calcium ethylate accelerated the oxidation lightly, if at all. Aluminum ethylate had no action.

The results obtained in this series of experiments indicated the surprising difference in the action of lead tetraethyl and the potassium and sodium ethylates compared with their action on gasoline.

Conclusion

It is to be noted also that only extremely small percentages of these compounds are necessary. It is here, then, that the engine-test evaluations of lead tetraethyl may best be compared with this slow oxidation method. It is unfortunate that at this writing no engine-test evaluations are available for the potassium and sodium ethylates. Aniline and diphenylamine, two substances with which the lead tetraethyl might have been compared, failed to have accelerating action in the liquid-phase oxidation.

It appears, then, that for a compound to have properties to be classed as a suitable antiknock, it must be an inhibitor of gas-phase oxidation and an accelerator of liquid-phase oxidation.

Compounds which fail to approach lead tetraethyl but which have some effect as antiknocks appear to have their effect only in one of the phases present in the gas engine at the temperatures tested.

The peculiar properties of lead tetraethyl and the aromatic amines in liquid-phase oxidation appear to be what might be expected from the work of Ormandy,⁷ who showed by the liquid droplet method in his determination of ignition temperatures that the amines raised and lead tetraethyl lowered such temperatures.

No attempt is made at this time to correlate these data with the mechanism of combustion in the gas engine. Lead tetraethyl by engine-test evaluation is the best antiknock substance. It may be due to ability to delay gas-phase oxidation and accelerate liquid-phase oxidation.

Summary

1. The oxidation of *n*-heptane in the gas phase appears not to be through its normal alcohol.

2. Heptyl alcohol may be oxidized only with difficulty in the gas phase. Lead tetraethyl has the ability to delay the accelerating action of butyl nitrite, but if once started the path of oxidation is the same as when not delayed.

3. Aniline, diphenylamine, lead tetraethyl, and potassium ethylate are all inhibitors of gas-phase oxidation.

4. There is no relation between the engine-test evaluation of inhibitors and the values obtained in their slow oxidation data for gas-phase oxidation.

5. Ethyl alcohol, aniline, diphenylamine, aluminum ethylate are not accelerators of liquid-phase oxidation.

6. Lead tetraethyl, and potassium and sodium ethylate are accelerators of liquid-phase oxidation when present in extremely small percentages.

7. Lead tetraethyl and potassium and sodium ethylate exhibit a surprising similarity of properties in affecting gas- and liquid-phase oxidation.

8. While slight absorptions of oxygen were obtained in certain of the tests, owing to the known instability of peroxides and the difficulty of definitely determining their presence, the authors believe that these data should not be considered as conforming or rejecting the peroxide theory of oxidation of hydrocarbons.

9. From the data presented it appears that an ideal antiknock substance might be obtained by incorporating a powerful inhibitor of only vapor-phase oxidation with a powerful accelerator of only liquid-phase oxidation.

Acknowledgments

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PARTIAL OXIDATION OF METHANE AND ETHANE IN THE PRESENCE OF CATALYSTS

T. E. LAYNG AND ROY SOUKUP

University of Illinois, Urbana, Illinois

The catalytic partial oxidation of various mixtures of methane and ethane with oxygen has been studied by the dynamic method at atmospheric pressure within the temperature range 100° to 700°C. Some experiments have also been made with a natural gas under similar conditions.

For the production of alcoholic or aldehydic intermediates, catalysts of copper and silver, oxides of these metals, activated charcoal, platinum oxide, and barium peroxide proved unsatisfactory on the basis of hydrocarbon consumed and products obtained.

Small amounts of nitrogen dioxide, when added to hydrocarbon-oxygen mixtures and passed through heated capillary tubes, were found to promote the oxidation materially. Yields of oxygenated derivatives varying from 15 to 30 per cent by volume of the amount of hydrocarbon used were obtained. As much as 38 per cent of the hydrocarbon has been decomposed in a single pass through the catalytic chamber.

Auxiliary catalysts used in conjunction with nitrogen dioxide activated the decomposition of intermediate oxidation products without materially increasing the amount of hydrocarbon decomposed.

Methyl nitrite has been shown to exert a promoting action in partial oxidation reactions of hydrocarbons.

An explanation is offered of the effect of small amounts of nitrogen dioxide and methyl nitrite on the partial oxidation of aliphatic hydrocarbons.

The hydroxylation theory of the combustion of hydrocarbons has been further confirmed by thermodynamic considerations as well as by experimental evidence.

On the basis of the hydroxylation theory of the combustion of hydrocarbons, some attempts have been made in the past to isolate alcohols, aldehydes, and acids by the partial combustion of a mixture of the hydrocarbon and oxygen or air. Natural gas is a prolific source of raw material for such processes, although other hydrocarbon-containing gases are also available. The products formed are extremely valuable for many purposes, either in the pure state or as mixtures.

Numerous patents have appeared in the literature, claiming the production of substantial amounts of these oxygenated derivatives, usually by a process comprising the passage of a mixture of hydrocarbon and air over a solid catalyst at an elevated temperature. A few¹ specify the use of gaseous catalysts. Published data are much more meager in quantity. It has been shown conclusively by Bone,² Wheeler and Blair,³ Medvedev,⁴ and Berl and Fischer,⁵ among others, that oxygenated derivatives could be formed by partial oxidation of gaseous hydrocarbons, although only traces of alcohols and acids were obtained. However, yields of aldehydes were too small to warrant the application of these processes to an industrial operation.

This investigation had for its object a study of the partial oxidation of mixtures of methane, ethane, and natural gas with oxygen under conditions which would yield the greatest amount of oxygenated derivatives, preferably the alcohols.

A thermodynamic analysis of the partial oxidation of methane and ethane, and hence natural gas in which these two hydrocarbons predominate, on the basis of Nernst's thermodynamic theorem, as well as by integration of available specific heat data, indicates that formaldehyde is the most probable product or reaction if the oxidation process is considered from a kinetic as well as a static aspect. This analysis, however, does not take into consideration the effect of catalysts in altering the reaction velocities of equilibria involved in partial oxidation, so that isolation of alcohols by direct oxidation of hydrocarbons is not impossible, though apparently difficult.

Experimental Procedure

In this investigation the catalytic partial oxidation of various mixtures of natural gas, methane, and ethane with oxygen was studied by the dynamic method at atmospheric pressure within the temperature range 100° to 700°C. The flow sheet of operation consisted essentially of the passage of an analyzed and measured quantity of a gas mixture through a heated reaction zone of small cross section, the times of heating being of the order of 0.1 to 1.0 second. Solid catalysts were mounted in the heated portion of the system, while gaseous catalysts were mixed with the influent gas before its

TABLE I
Data for solid catalysts: single-pass apparatus

	Catalyst									
	Copper		Copper oxide	Silver oxide	Barium peroxide	Platinum oxide		Activated charcoal		
Temperature, °C	400	570	500	605	520	400	520	410	610	
Influent gas ^a :										
CO ₂	0	0.3	0.4	0.2	0.5	0	0	0.3	0.3	
O ₂	29.0	4.4	28.8	23.4	18.1	18.4	18.4	18.2	18.2	
H ₂	0	0.1	0	0	0	0	0	0	0	
CO	0.2	0.2	0.2	0.1	0.1	0.2	0.2	0.3	0.3	
C ₂ H ₆	15.0	21.9	15.6	17.2	18.2	18.6	18.6	19.2	19.2	
CH ₄	47.6	67.3	45.6	52.9	58.4	58.8	58.8	57.5	57.5	
N ₂	8.2	5.8	9.4	6.1	4.7	4.0	4.0	4.5	4.5	
Rate of flow of gas, cm/sec	161	121.2	28.9	30.5	27.6	8.3	7.9	3.4	2.5	
Time of heating, seconds	0.09	0.12	0.52	0.49	0.54	1.81	1.90	4.41	6.00	
Effluent gas:										
CO ₂	0	1.4	0.5	0.2	0	11.9	11.7	1.8	9.8	
C _n H _{2n}	0	0	0	0	0	0	0	0	0.3	
O ₂	28.0	1.8	27.8	23.0	18.5	0.3	0.3	15.0	0.5	
H ₂	0	0	0.1	0	0.2	0	0	0.1	0.7	
CO	0.5	0.2	0.2	0.1	0.3	0.1	0	0.8	7.2	
C ₂ H ₆	14.7	21.5	14.2	16.8	17.2	15.6	15.9	15.9	18.7	
CH ₄	46.6	66.1	45.1	52.6	57.7	65.5	65.0	61.8	57.1	
N ₂	10.2	9.0	12.1	7.3	6.1	6.6	7.1	4.6	5.7	
Contraction:										
Influent gas, cc	198.7	200.0	200.0	200.0	199.1	199.9	200.0	200.0	200.0	
Effluent gas, cc	197.6	196.3	197.8	198.6	196.1	176.5	175.4	198.3	190.4	
Contraction, cc	1.1	3.7	2.2	0.4	3.0	23.4	24.6	1.7	9.6	
" <i>n</i> -Factor:" ^b										
Influent gas						1.245	1.245	1.250	1.250	
Effluent gas						1.180	1.197	1.205	1.250	

^a All gas analyses are reported on the dry basis. Both initial and final gases, however, were saturated with moisture while in the single-pass apparatus.
^b "*n*-Factor" is an index of the relative amounts of ethane and methane in a mixture of these two gases, as determined by gas analysis.

admission into the reaction chamber. After passage through this chamber, the effluent gas was rapidly cooled, intermediate products were removed by condensation and scrubbing, and the gas was then passed into a reservoir where it was accurately measured and analyzed. Initial and final gas compositions were determined by analysis in a modified Orsat apparatus. In the analysis of intermediate products from methane oxidation, formic acid was determined by a permanganate titration⁶ of residual liquors after removal of formaldehyde and methanol by distillation. No quantitative analyses were made of the condensate and wash water obtained by the oxidation of natural gas and ethane, since the amounts of effluent gases utilized were too small to permit quantitative methods to be applied. When acidic gaseous catalysts were used, it became necessary to effect the removal of inorganic acids formed by partial solution of these catalysts in the condensates and scrubbing liquors before analyzing for alcohols, aldehydes, etc. Formaldehyde was determined separately in an aliquot part of the distillate obtained by neutralizing the combined condensate and wash water and removing formaldehyde and methanol by distillation. The aldehyde was determined either by the iodometric⁷ or hydroxylamine hydrochloride⁸ titration methods. Methanol was estimated from the amount of standard permanganate solution required for the oxidation of both methanol and formaldehyde in another similar portion of the distillate.⁹

Results with Solid Catalysts

Catalysts consisting of copper and silver films which were mounted in a narrow annular space in such a manner as to provide an intimate contact between the influent gas stream and the catalyst, as well as to obviate the difficulties of heat transfer which are involved in the case of catalysts supported in the usual manner on pumice, asbestos, etc., did not promote the oxidation to intermediate products successfully in single passes through the catalytic chamber. Oxides of copper and silver, supported as in the case of the metals, exhibited better promoting action than the latter, but the reaction was still slight under conditions which favored the production of intermediates.

Barium peroxide at 450°C, supported on asbestos, proved to be an unsatisfactory promoter of the partial oxidation reaction for single-pass operations.

A platinum oxide catalyst, supported on asbestos, caused appreciable oxidation of natural gas to occur at temperatures in excess of 400°C, but this oxidation proceeded completely toward

the production of carbon dioxide and water. Practically all of the oxygen present when using a mixture of oxygen, ethane, and methane in the proportions by volume of 1:1:3 was utilized in a single pass through the catalytic chamber in a heating time of about 2 seconds. By "heating time" is meant the time required for one molecule of the influent gas to pass in a straight line from one end of the heating zone of the catalytic chamber to the other.

Activated charcoal gave results which were of about the same order as those obtained by the use of copper and silver. However, at the temperatures required for appreciable reaction to occur, the charcoal was itself oxidized to carbon monoxide and carbon dioxide.

Results with Gaseous Catalysts

Catalysts employed in the vapor phase gave varying degrees of success in promoting the partial oxidation of gaseous hydrocarbons of the paraffin group. Sulfur trioxide in amounts of about 1.0 per cent by volume failed to accelerate the oxidation reaction in single-pass operation.

Nitrogen dioxide, when present in amounts of from 0.3 to 5.0 per cent by volume, exerted considerable promoting action in the oxidation of mixtures of the hydrocarbon and oxygen when passed through a capillary tube of Pyrex glass or fused quartz heated to 600°–700°C. The accelerating effect of nitrogen dioxide increased as the amounts of that gas in the initial gas mixture were increased, yields of oxygenated derivatives varying from 15 per cent to 30 per cent by volume of the hydrocarbon used were obtained. The higher yields were obtained by recirculation of gases through the catalytic chamber, oxygen being added to maintain a suitable hydrocarbon–oxygen ratio. A single pass through the heated zone of the system resulted in a decomposition of the hydrocarbons in natural gas to the extent of 35 to 84 per cent in the case of ethane and 0.2 to 50.5 per cent in the case of methane, while the yield of oxygenated derivatives varied from 0.6 to 20.3 per cent of the total hydrocarbon, depending on the experimental conditions. It was found that a temperature of at least 600°C and a heating time of about 0.5 second were necessary to obtain satisfactory yields.

Effect of Auxiliary Catalysts with Nitrogen Dioxide

Some experiments, in which an activated charcoal and a platinum oxide catalyst were employed in conjunction with nitrogen dioxide, indicated that the use of these materials resulted

in a decrease in the amount of oxygenated derivatives formed and an increase in yield of hydrogen, oxides of carbon, and steam. These auxiliary catalysts evidently activated the oxidation (or decomposition) of intermediate products of partial combustion under the experimental conditions used.

At temperatures of 600° to 700°C and a heating time of about 1.5 seconds the oxidation of pure methane and ethane was also materially promoted by the presence of small amounts of nitrogen dioxide in the influent gas. Yields of oxygenated derivatives were increased about thirtyfold in a

single pass by the addition of 1 per cent of nitrogen dioxide to a gas mixture containing 27.5 per cent oxygen, 17.4 per cent ethane, and 52.1 per cent methane. In all cases where nitrogen dioxide was employed as a catalyst the amounts of carbon dioxide obtained in the effluent gases were uniformly much smaller than the corresponding amounts of carbon monoxide and hydrogen, indicating that the oxidation proceeded only to a small extent to the carbon dioxide-water stage. Although an increase in the rate of gas flow resulted in the formation of greater amounts of oxygenated derivatives in relation to

TABLE II
Data for gaseous catalysis: single-pass apparatus

	Catalyst							
	SO ₃		NO ₂ (Pyrex catalytic chamber)					
Temperature, °C	440	635	600	635	632 ^a	700	620	620
Influent gas ^a :								
CO ₂	0.5	0.5	0.2	0.2	0.2	0	0	0
O ₂	18.4	18.4	20.6	48.0	27.5	26.2	10.0	30.6
H ₂	0	0	0	0	0	0	0	0
CO	0.2	0.2	0.1	0.2	0.2	0.2	0	0
C ₂ H ₆	16.9	16.9	18.3	10.9	17.4			
CH ₄	52.1	52.1	56.3	34.0	52.1	61.2	38.4	20.4
N ₂	11.9	11.9	4.5	6.7	2.8	12.4	51.6	49.0
Rate of flow of gas, cm per second	11.7	12.3	4.7	8.3	8.65	8.55	8.64	8.49
Time of heating, seconds	1.28	1.22	3.2	1.81	1.74	1.76	1.74	1.77
Effluent gas:								
CO ₂ ^b	3.1	3.2	2.0	5.1	0.9	1.4	0.3	0.8
C _n H _{2n}	—	—	0.5	—	—			
O ₂	17.9	17.3	0.6	5.5	25.0	2.2	6.0	20.2
H ₂	0	0.2	4.4	7.8	0.3	7.5	0.9	0.8
CO	0.1	0.3	15.0	39.3	0.9	18.7	1.8	7.0
C ₂ H ₆	14.1	14.0	7.5	2.6	15.9			
CH ₄	51.0	51.5	58.5	25.3	50.2	50.0	34.4	13.7
N ₂	13.8	13.5	11.5	14.4	6.8	20.0	56.6	57.5
Contraction, cc ^c	1.4	0.1	32.1	64.4	2.6	32.0	11.8	26.3
Per cent hydrocarbon decomposed:								
Ethane	—	—	67.0	84.0	9.8	35.6	21.2	42.0
Methane	—	—	14.0	50.5	5.7			
Per cent of total hydrocarbon converted to oxygenated derivatives	—	—	20.3	12.0	0.6	9.9	12.7	9.0
Per cent of catalyst present, by volume	0.6	1.25	1.4	0.35	0	0.6	1.2	1.2

^a NO₂ absent from influent gas.

^b Includes any of gaseous catalysts which remained in effluent gas after scrubbing and was therefore removed as "CO₂" in KOH absorption pipet.

^c Resulting from passing influent gas through catalytic chamber.

the yield of carbon monoxide and hydrogen, yet the total oxidation was less, thus necessitating recirculation.

Addition of about 5.0 per cent by volume of hydrogen chloride to the influent gas caused some activation of the partial combustion reaction, but to a less degree than nitrogen dioxide. In every case the promoting action of hydrogen chloride was less than that obtained by Medvedev,⁴ a condition which probably is explained by the additional contact catalysts employed by Medvedev.

Methyl Nitrite as Catalyst

Methyl nitrite in amounts of 1.0 to 2.0 per cent by volume were also shown to exert a promoting

action less vigorous than that of nitrogen dioxide but more pronounced than that of other catalysts investigated under approximately similar operating conditions. The action of methyl nitrite was probably based on its spontaneous decomposition at elevated temperatures into nitrogen dioxide or nitric oxide and a carbon-hydrogen-oxygen residue, the former acting as the catalyst.

Explanation of Promoting Action of Nitrogen Dioxide and Methyl Nitrite

In order to obtain data on the character of oxygenated derivatives formed in these reactions, experiments on a larger scale were necessary, utilizing a semi-continuous apparatus as mentioned previously. In a typical series of experi-

TABLE III
Data for gaseous catalysts: semi-continuous apparatus

	Catalyst				
	NO ₂ (Pyrex catalytic chamber)				
Temperature, °C	690	690	690	690	690
Influent gas:					
CO ₂	0.4	1.5	4.2	8.2	8.2
O ₂	25.2	19.7	16.5	9.2	7.6
H ₂	0	6.0	8.9	10.4	10.2
CO	0.4	18.0	29.4	39.2	44.9
CH ₄	69.5	46.0	30.0	20.3	18.6
N ₂	4.5	8.8	11.0	12.7	10.5
CH ₄ :O ₂	2.76	2.34	1.82	2.21	2.45
Time of heating, seconds	1.81	1.88	1.90	1.90	1.81
Effluent gas:					
CO ₂	2.0	5.4	9.5	8.2	12.4
O ₂	0	0	0.1	4.9	0.2
H ₂	11.2	14.7	15.5	11.2	15.8
CO	20.9	32.4	40.0	42.0	44.0
CH ₄	55.4	34.5	21.5	19.4	11.4
N ₂	10.5	13.0	13.4	14.3	16.2
Volumes:					
Influent gas, cc	14,270	12,530	12,290	10,340	10,183
Effluent gas, cc	11,059	11,319	10,181	10,032	9,505
Contraction, cc	3,210	1,211	2,112	310	678
Per cent methane decomposed	38.2	32.2	40.7	7.3	42.6
Per cent methane converted to oxygenated derivatives:					
Per experiment	13.1	0.2	7.0	0.12	11.3
Yields of oxygenated derivatives per liter of methane decomposed, by analysis:					
Methanol, mg					25
Formaldehyde, mg					205
Formic acid, mg					76

ments, using pure methane as the hydrocarbon source, four passes of the gas through the system, adding oxygen before each pass in order to maintain a constant oxygen-hydrocarbon ratio, resulted in a yield of oxygenated derivatives amounting to 25 mg methanol, 205 mg formaldehyde, and 76 mg formic acid per liter (standard conditions) of methane decomposed. This was equivalent to 0.0093 atom carbon per liter of methane decomposed. Of the original amount of methane present, 80.3 per cent was decomposed in four passes, while 27.1 per cent appeared as oxygenated derivatives. Calculations indicated that 0.0151 atom of carbon per liter of methane decomposed should have been obtained, whereas only 0.0093 atom, or 61.5 per cent, was experimentally determined to have been present.

The actual yield of oxygenated derivatives was probably decreased by decomposition reactions which took place in the condensate and scrubber during the run, since nitric acid was continuously present on account of the partial solution of nitrogen dioxide in water. In fact, if the condensate temperature was allowed to rise to room temperature, it was observed that an ebullition occurred within the liquid, indicating a decomposition reaction which resulted in the formation of a gas. Among these oxidations may have been those of formaldehyde and methanol to formic acid, as well.

It is improbable that the pronounced action of small amounts of nitrogen dioxide in accelerating the partial oxidation of gaseous hydrocarbon-oxygen mixtures was a result of the formation of unstable intermediates by chemical reaction of the hydrocarbon and nitrogen dioxide. A more satisfactory explanation was sought in the readiness with which nitrogen in its oxides changes its valence, thus giving an opportunity for the accomplishment of adsorption phenomena of some character. In any case, the action of nitrogen dioxide appeared to be an additional example of homogeneous catalysis in the gaseous phase, for changing the composition of the chamber in which the catalysis occurred had apparently no effect on the nature of the reaction. Moreover, the rate of oxidation obtained in the small single-pass unit agreed closely with rates

and degrees of oxidation obtained in the larger semi-continuous apparatus.

For the purposes of this investigation it suffices to indicate that the promoting action of small amounts of nitrogen dioxide in partial oxidation of hydrocarbon-oxygen mixtures is far superior to that of the other solid and gaseous catalysts which were investigated. Moreover, the yields of oxygenated derivatives obtained were about double the amounts which the best⁴ of previous investigations on the basis of single-pass oxidation was able to indicate, and were many times larger than the yields secured by Wheeler and Blair³ in a circulation apparatus.

Tabulated Results

Tables I to III show representative results obtained with variable gas-oxygen mixtures at different temperatures under the influence of different catalysts. One hundred and fourteen tests were made in all. These results are most easily considered by noting the changes in percentages of carbon monoxide, the contraction in volume, the "*n*-factor," and the percentage of total hydrocarbons converted to oxygenated derivatives under the varying conditions.

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RELATIVE RATES OF REACTION OF OLEFINS IN COMBUSTION WITH OXYGEN AND IN OXIDATION WITH AQUEOUS POTASSIUM PERMANGANATE*†

HAROLD S. DAVIS‡

Massachusetts Institute of Technology, Cambridge, Massachusetts

With a view to investigating the relative rates of combustion of the olefins, known mixtures of ethylene and propene and of ethylene and isobutene were exploded with oxygen, and the proportion of each olefin remaining unburned was found by analysis of the products. One slow combustion was also made of a mixture of ethylene and isobutene. In every case propene or isobutene burned faster than ethylene.

To test their relative ease of oxidation by potassium permanganate, known mixtures of ethylene and isobutene were dissolved in water and oxidized by a deficiency of permanganate. Then the proportion of each olefin unoxidized was found by boiling out the gases and analyzing them. Here again isobutene reacted faster than ethylene.

Calculations of the relative rates of reaction based on a formula developed by Francis, Hill, and Johnston are given.

Relative Rates of Combustion with Oxygen

Apparatus. Fifty cubic centimeter samples of the gas mixtures were exploded over water in upright thickwalled Carius tubes (or similar ones of Pyrex glass). The upper end of the tube was closed by a rubber stopper (wired in) through which passed two glass tubes carrying platinum or tungsten electrodes and an exit tube with a glass stopper. The inner surface of rubber exposed was small and was always wet with water before the explosion. It showed no signs of oxidation. The lower end of the tube was connected with a water-leveling bulb.

In the experiments recorded here the combustions were always incomplete, both olefins and oxygen being found in the products. The passage of the flame through the tube was clearly marked and the detonations very mild. It was hoped that these conditions would favor differential combustion of the olefins.¹

The apparatus used in experiment 7 for the slow combustion of a nonexplosive mixture of ethylene and isobutene is shown in Fig. 1.

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‡ Director and research associate, Project No. 19.

Materials. Commercial "refined" ethylene in a steel cylinder from a well-known firm was used. It dissolved only very slowly in 86 per cent sulfuric acid and was 99.5 per cent soluble in bromine water.

Propene was prepared by adding phosphorus pentoxide slowly to well-cooled and well-stirred C.P. isopropanol and heating the product.

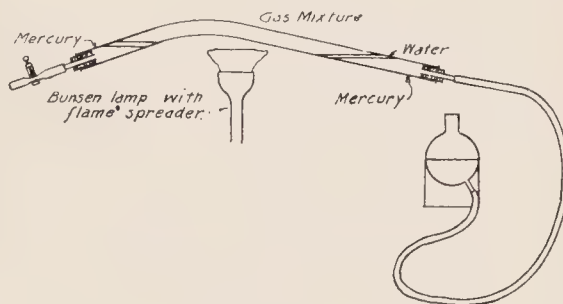


FIG. 1. Apparatus used in experiment 7 for combustion of a nonexplosive mixture of ethylene and isobutene.

Isobutene was made from tertiary butanol (m.p. 16°C and miscible with water without any cloud) by dehydration with oxalic acid at about 95°C.

Commercial oxygen made from liquid air was used.

All the gases were well washed with water.

Procedure for Analysis. Carbon dioxide was determined by absorption in caustic alkali in the usual manner.

Propene and isobutene were measured by absorption with 86 per cent sulfuric acid to constant volume. The separation from ethylene, which remains undissolved, is very sharp in the

TABLE I
Inflammation or slow combustion of olefin-oxygen mixtures

Mixtures							
Ethylene, Propene, Oxygen				Ethylene, Isobutene, Oxygen			
Experiment	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Original mixture, per cent by vol.	C ₂ H ₄	20.6	21.7	9.9	C ₂ H ₄	10	23.0
	C ₃ H ₆	17.8	21.8	29.9	C ₄ H ₈	27	18.8
	O ₂	53.6	50.5	58	O ₂	60	50.0
Vol. (C _n H _{2n}) × (n/2) ^a Vol. (O ₂)					0.9	0.8	0.5
Appearance of combustion	Flash, no carbon	Flash, no carbon	Deep, purple flame, carbon deposit	Gentle flash, carbon deposit	Lurid flame, carbon deposit	Light flash at top only of tube	No explosion but slow combustion, no carbon
	73	86	69	52	36	22	28
	89	100	100	72	86	37	53
Percentage consumed	C ₂ H ₄	—	97	79	97	—	62
	C ₃ H ₆	—	—	—	—	—	—
	O ₂	—	—	—	—	—	—

^a Mixtures contain proportions of oxygen corresponding with C_nH_n + (n/2)O₂, yield on explosion mainly carbon monoxide and hydrogen, without separation of carbon or material steam formation. Bone and Townend, *Op. cit.*, p. 394.

TABLE II

A—O₂ (gas) used up, as shown by analysis before and after combustion.
 B—O₂ in CO and CO₂ of gaseous products.
 C—O₂ necessary to unite with all the C in olefins used up, to give the CO₂ actually found and CO (or formaldehyde).

Experiment	A	B	C
	cc	cc	cc
1	41.8	41.8	44.0
3	49.0	46.1	48.6
4	46.0	41.1	41.3
5	58.2	49.4	55.4
7	27.8	18.2	32.8

case of isobutene, but is less satisfactory for propene.

The ethylene residue in the gas was measured by absorption into saturated bromine water, then oxygen by pyrogallol, and carbon monoxide by acid cuprous chloride.

The only data essential for the problem under investigation were the volumes of the two olefins and of the oxygen in the gas mixture before and after combustion. However, the other measurements were useful to check the conclusions.

Table I, which summarizes the experiments, shows that in every case propene or isobutene burned faster than ethylene with oxygen.

It is known that olefins undergo thermal decomposition in flames and any acetylene thus produced would be counted as ethylene in the method of analysis employed. However, except possibly in the case of highly endothermic ones such as acetylene, which decompose explosively at high temperatures or under shock, the rate at which hydrocarbons combine with oxygen far exceeds that at which they decompose in flames.²

The data in Table II indicate that thermal decomposition of the olefins played only a minor part in these experiments. Practically all the carbon from the olefins used up was to be found in oxygenated products (CO₂, CO, and CH₂O).

Relative Rates of Reaction with Aqueous Potassium Permanganate

Procedure. To prepare a water solution containing known quantities of ethylene and isobutene, 100 cc of an analyzed mixture of the two gases were forced into the reaction chamber A (Fig. 2) full of water. The displaced water rose up into D.

After vigorous stirring the residual gas was withdrawn and the quantities of ethylene and isobutene in it were determined by analysis. The volumes of olefins dissolved by the water were calculated.

This water in the flask was then rapidly stirred and a solution of potassium permanganate slowly added, the total quantity being insufficient to oxidize all the dissolved olefins. At the rate used (about 1 cc of nearly saturated solution per minute) the permanganate color penetrated into the rapidly moving water only about 3 cm. from the inlet. It was noticed, however, that if the rate was increased the violet permanganate color would permeate almost the entire solution, disappearing like a flash when the feed was cut off.

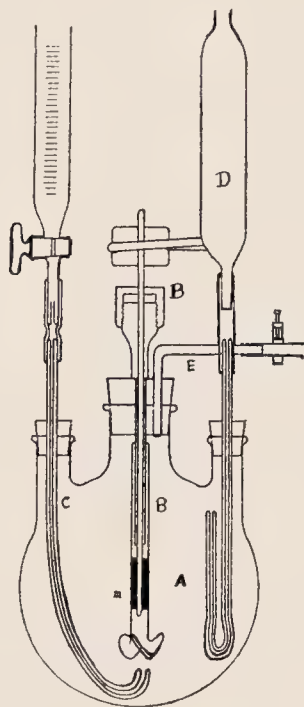


FIG. 2. Apparatus for competitive oxidations of olefins by permanganate in aqueous solution.

A—1000-cc flask completely filled with a water solution of olefins.

B—Stirrer system provided with a gas-tight stuffing box at the top. The glass stirrer tube is cemented to the propeller shaft at *m* and the glass tube extends up around the shaft bearing. Any gas leakage must first pass down the narrow space between these tubes and can therefore be seen at once.

C—Inlet tube for delivering gases, or permanganate solution directly under stirrer blades.

D—Water overflow system designed to prevent escape of gases.

E—Exit tube for gases.

It was therefore concluded: (1) that the stirring was good, although difficult in a vessel completely full, and that for the most part the permanganate was in contact with an excess of dissolved olefins, so that the latter must have really competed for the oxidizing agent; (2) that the reactions, although rapid, were by no means instantaneous, since the color could be made to permeate the whole solution.

After oxidation, the water in the reaction chamber was boiled out directly from the flask without venting to the air and the evolved gases were collected over mercury. A considerable quantity of water was also displaced partly by expansion and partly by priming. In the last three experiments this water was collected in an evacuated flask placed between the reaction chamber and the gas buret. After the reaction chamber had been thoroughly boiled out, it was shut off and the intermediate flask also boiled out so that all the gases, including some air, were collected over a minimum of water. The volumes of ethylene and isobutene in these gases were found by analysis.

The reaction chamber was not placed in a constant-temperature bath. Room temperature was about 23°–24°C.

The results are summarized in Table III. In every case a greater proportion of isobutene than of ethylene was oxidized.

Calculations. Values of the ratios of the reaction coefficients, assuming the reactions to be of the second order, show fair agreement.

TABLE III

Oxidation in water solution by permanganate:
ethylene *vs.* isobutene

No.		Before oxidation	After oxidation	Oxidized	
		cc.	cc.	cc.	Per cent
8	Ethylene	35.7	19.4	16.3	45.6
	Isobutene	34.9	15.6	19.3	55.3
9	Ethylene	38.2	20.9	17.3	45.3
	Isobutene	40.1	15.5	20.6	61.4
10	Ethylene	33.1	0.16	32.9	99.4
	Isobutene	32.3	0.0	32.3	100
11	Ethylene	27.8	6.3	21.5	77.3
	Isobutene	28.5	1.4	27.1	95.1

The following calculations of the relative rates of reaction of the olefins in the two series of tests were made for those experiments in which each of the two olefins competing for the reagent was incompletely oxidized. They are based on the formula developed by Francis, Hill, and Johnston³ for the case where two substances compete (in irreversible reactions of the second order) for a third substance:

$$\frac{K_A}{K_B} = \frac{\log (1 - r_A)}{\log (1 - r_B)},$$

TABLE IV

Relative rates of reaction of olefins

Combustion with oxygen				Oxidation with aqueous permanganate	
Expt.	<i>K</i> propene	Expt.	<i>K</i> isobutene	Expt.	<i>K</i> isobutene
	<i>K</i> ethylene		<i>K</i> ethylene		<i>K</i> ethylene
1	1.68	5	4.4	8	1.32
4	1.73	6	1.9	9	1.57
		7	2.3	11	2.03
Average	1.71		2.8		1.64

Ratios of Relative Rates

	Combustion with oxygen	Oxidation by aqueous permanganate
Ethylene	1	1
Propene	1.7	—
Isobutene	2.8	1.6

where r_A and r_B = fractions of olefins A and B which react; and K_A and K_B = velocity constants of oxidation reactions of the two olefins.

The values for the separate experiments and the average values are summarized in Table IV.

Comparison of Reactions with Oxygen and with Bromine

There are certain striking analogies between the reactions of olefins with oxygen and with bromine:

(a) Ethylene reacts more slowly than propene or isobutene in the following cases: (A) bromination in carbon tetrachloride solution⁴; (B) combustion with oxygen; (C) oxidation with aqueous permanganate.

(b) In bromination of the olefins the main action is bromine addition to the unsaturated carbon atoms. In combustion there is good evidence that the primary reactions are the addition of one or two atoms of oxygen to the olefin.⁵

(c) The rates of combustion⁶ and of bromination⁴ of olefins can both be decreased by intensive drying.

These analogies perhaps justify the suggestion that the natures of the groups attached to unsaturated carbon atom affect, through the same mechanism, the number of the molecules in the olefins which become active in unit time both for bromination and oxidation. The nature of that mechanism which concerns the atoms in the olefin molecules remains to be shown.

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6. *Ibid.*, Chap. XXIV.

Second Symposium on Combustion

This symposium was held by the Division of Gas and Fuel Chemistry, with the cooperation of the Divisions of Industrial and Engineering Chemistry, Petroleum Chemistry, and Physical and Inorganic Chemistry, at the Ninety-fourth Meeting of the American Chemical Society, Rochester, New York, September 9-10, 1937.

INTRODUCTION TO THE SYMPOSIUM. THE DEVELOPMENT OF COMBUSTION RESEARCH AND THE PRESENT OUTLOOK*

BERNARD LEWIS

Explosives Division, Pittsburgh Experiment Station, U.S. Bureau of Mines, Pittsburgh, Pennsylvania

Nine years ago the Division of Gas and Fuel Chemistry of the American Chemical Society, jointly with the Division of Petroleum Chemistry, sponsored a symposium which was essentially on gaseous combustion. [That symposium was held at the Seventy-sixth Meeting of the American Chemical Society, held at Swampscott, Massachusetts, September 10-14, 1928]. The present symposium reflects the progress in combustion research made since then. Three divisions may be distinguished in this research. One includes the chemistry and kinetics of slow and explosive oxidation reactions. Another is the propagation of flame with the establishment of boundaries between burnt and unburnt gases. A third consists of a study of the state of the burnt gas, that is, the establishment of thermodynamic equilibrium and temperature gradients. In a number of technical problems such as are presented by internal-combustion engines, problems in more than one of these divisions occur.

The time limitations that are unavoidably placed on the present large program and other circumstances have prevented the inclusion of contributions from many active investigators both here and abroad. It is regretted that it was not possible to obtain a representative group of contributions in the exceedingly important and active field of catalytic combustion. The problem of the diffusion flame was ably treated at the earlier symposium, and it has been omitted from this one since little could be added at this time

that would contribute to a further understanding of the subject. The subject of the detonation wave, which in the main is a physical problem in hydrodynamics, has also been omitted, since it had already reached an advanced stage of theoretical development. Some more recent discoveries in this field, such as the discontinuous progress of the detonation wave and the spinning detonation in which a spiral track is described by the wave front, merit further study. It does not appear that problems of technical interest are involved.

Certain fundamental lines of development are indicated by the present accomplishments in the various divisions of the symposium. Ultimately, it is desired to understand fully the intricate chemistry and kinetics of the oxidation of combustibles. In the case of hydrogen we are probably not very far from this realization. This can also soon be said of carbon monoxide. The reactions of hydrocarbons are much more complicated. There is a well-founded suspicion that the key to the chemistry and kinetics of hydrocarbon oxidation lies in the formation and decomposition of peroxidic substances. The subject of the complicated and extremely important heterogeneous reactions of hydrocarbons is a field of study in itself. It can be stated with some assurance that there is hardly a case of slow oxidation or of the establishment of a critical condition leading to ignition, as, for example, in engine knock, that does not involve surface reactions of some kind. The function of the interface between gas and fuel droplets as the possible initiator of ignition in the diesel engine should not be overlooked and deserves study. Thus, the oxidation of

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organic substances offers challenging problems to the kineticist. Such studies should stimulate research and technical development in many directions, possibly much more than we can foresee now.

There are a number of problems encountered that are of such extreme complexity that a rational and immediate scientific solution seems to be quite impossible. Sometimes they are of such practical importance that something has to be done about it, despite the impossibility of a quantitative scientific analysis of the problem or even of the guiding principles that are involved. A perplexing problem of this sort is that of fuel rating. Nevertheless, one must admire the practical progress that has been made in this work. It is in the nature of the problem that the methods of rating fuels developed thus far are not entirely satisfactory, and that their shortcomings become more pronounced as the limits of tolerance in fuel specifications narrow. If active investigators in this field were asked today whether they could improve on the principles of present fuel rating practice, the answer would probably be in the negative. They would protest that they have not even as assured qualitative knowledge of the processes that occur between the fuel, the air, and the surface in the engine; much less could they give a quantitative estimate of the likelihood of knock in the Otto engine or of the length of the preignition period in the diesel engine. There is, however, nothing to suggest that the problems are insoluble.

Among other problems of great complexity are those of ignition by a local source such as a spark and of the propagation of flame. In the approach to both problems the older idea that only the transfer of heat need be considered the decisive element must now give way to the inclusion of the migration of chain carriers and the various kinetic aspects of chain development. There will be presented in this symposium pertinent experiments pointing to the role of chain carriers, and also a first attempt at a mathematical analysis of

the dual problem of heat flow and diffusion of chain carriers. In safety practice the specification of an admissible spark would be materially aided by a deeper understanding of the action of the spark on a combustible mixture. A similar situation exists with respect to the problem of flame propagation which entails limits of inflammability, the latter being of utmost practical importance in hazardous industrial operations.

Whether mine and other explosions can be effectively inhibited by some means such as the addition of small amounts of substances acting as negative catalysts to the reaction chain development, remains to be answered in the future. However, there is no question but that present knowledge can materially aid in the elimination of thousands of explosion hazards that today lurk below and above ground all over the country.

A much clearer description of the state of the burnt gas that emerges from the flame can now be given than was possible ten years ago. The essential tool to study the burnt gas has been provided by band spectroscopy, in the form of accurate data of energy contents (specific heats) and equilibrium constants. It has become possible to establish order in this field, which has admittedly been in a confused state even since it was first touched upon by Bunsen. It has been shown that the flame effects a potent transformation of the combustible mixture to practically thermodynamic equilibrium, leaving no room for large hidden sources of energy in the form of latent heat. There are, however, certain problems that should be studied further, such as the anomalous effects that appear as a time-dependence of specific heats and the study of flames of very rich mixtures of organic combustibles where complicated and partly unknown dissociation equilibria exist.

No doubt we all shall learn and profit from the present gathering. It is hoped that the impetus given by the work presented will stimulate further research along both experimental and theoretical lines.

CHEMICAL ACTION IN THE GLOW DISCHARGE XV. REACTIONS PRECEDING IGNITION

A. KEITH BREWER

Bureau of Chemistry and Soils, U.S. Department of Agriculture, Washington, D.C.

Unusual opportunities for the study of the factors underlying ignition are offered by the glow discharge, since within the discharge are to be found positive ions, atoms, excited molecules, and electrons of known energy content. All of these are present under conditions fairly well known and controllable by the investigator.

The glow discharge may be produced in a cold electrode tube at pressures ranging from a hundredth of a millimeter to several centimeters. The discharge itself consists of the Crookes dark space adjacent to the cathode, followed in order by the negative glow, the Faraday dark space, and the positive column which extends to the anode. Any of these regions, except the Crookes dark space, may be eliminated by moving the anode towards the cathode, without changing the characteristics of the remaining regions.

The potential drop across the Crookes dark space is 300 volts or more, depending on the conditions of the experiment, the actual gradient often being 1000 volts per centimeter. The length of the dark space is about one-half a mean free path between ionizing collisions for an electron of energy corresponding to the cathode potential drop. The potential drop in the negative glow is negligible. The length of the negative glow in various gases corresponds exactly to the range of electrons possessing an energy equal to the full cathode potential drop as given by Lehmann.⁴ This makes it possible to use directly the data of Lehmann in computing the number of positive ions formed per electron in the negative glow.

The Faraday dark space is a low energy region in which the electrons leaving the negative glow are accelerated until they reach the ionization potential of the gas, at which point the positive column sets in. The gradient in the Faraday dark space is usually of the order of 20 to 25 volts per centimeter. The positive column is a region of low energy ionization. The average energy of the electron is from 6 to 8 volts, indicating that the maximum energy does not materially exceed the ionization potential. The gradient is of the order of 15 to 20 volts per centimeter.

Chemical reactions which may be produced in the glow discharge are of two general types, propagating and nonpropagating. Under controlled conditions it is possible to study the reaction in explosive mixtures without propagation. By varying the conditions of the experiment, reaction chains can be introduced to study the

factors influencing the reaction through various degrees of propagation until ignition occurs.

A detailed description of the various reactions studied has been presented in a series of articles.¹

Nonpropagating Reactions

Typical reactions studied under nonpropagating conditions are the synthesis of ammonia, the oxidation of nitrogen, the formation of ozone, the oxidation of hydrogen, the oxidation of carbon monoxide, and the oxidation of methane. The decomposition of ammonia, nitrogen dioxide, nitrous oxide, water, methane, and carbon monoxide have also been studied. It should be pointed out that in these studies conditions were so arranged that only the forward reaction was in evidence; any possible back reaction was completely, or almost completely, eliminated from the experiment.

Since all these reactions as they occur in the discharge possess marked similarities in character, the various factors influencing the rate of reaction will be described for the entire series, rather than for individual cases.

Portion of the Discharge in Which the Reaction Occurs. The Crookes and Faraday dark spaces appear incapable of inducing reactions. All reactions occur readily in the negative glow except the synthesis of ozone, failure in this case being apparently due to the difficulty in eliminating the back reaction. Under no conditions has it been possible to ignite explosive mixtures in the negative glow, although slight evidence of chains was observed at high current densities. In the positive column both propagating and nonpropagating reactions may be produced; at low current densities chains are inappreciable even in the most explosive mixtures.

Effect of Pressure. The rate of reaction in the negative glow is independent of the pressure over the range investigated (20 mm to 0.2 mm). The characteristics of the glow are difficult to control over a greater pressure range. The absence of a pressure effect shows the reactions to be of zero order. In consequence it is possible to state definitely that the reaction must be initiated by specific reaction centers, rather than by regions of high energy density. In addition it is evident that any state which is in equilibrium with any other state does not participate in the reaction;

thus the reaction $A + B_2 \rightarrow AB_2$ will show a pressure coefficient if an $A_2 \rightleftharpoons 2A$ equilibrium exists in the gas.

Effect of Current. The rate of reaction is proportional to the current over as wide a range as can be studied. The immediate interpretation of this fact is that the reaction is initiated by specific reaction centers, formed presumably by direct electron impact. Interaction between these primary reactive states, or conditions involving the interaction of primary with other excited states formed in the discharge, can be eliminated from the reaction mechanism; likewise the formation of initial reactive centers by the interaction of non-reactive primary states can be excluded; all of these possibilities require the rate to be dependent on some higher power of the current.

The rate of production of positive ions in the discharge is known to be independent of the pressure, and proportional to the current over the region where the voltage remains constant. The intensity of the characteristic spectrum of the discharge indicates that the concentration of atoms and excited molecules is dependent on the pressure and the current density. Direct measurements of the atom concentration in the discharge by Crew and Hulburt³ also confirm this contention. The natural conclusion to be drawn, therefore, is that the initial reaction centers are positive ions formed by direct electron impacts.

Effect of Temperature. Reactions in the negative glow are unique in that they possess either a zero or a negative temperature coefficient. Even the oxidation of hydrogen occurs at the same rate over a 400°C change in temperature. The complete absence of a positive temperature coefficient is of particular significance in this study of the nature of the initial reaction centers, since it shows that these centers contain within themselves all the energy necessary for reaction. Reaction occurs, therefore, between the original active centers and normal molecules.

Effect of Added Gases. In syntheses the rate of reaction is always accelerated by the addition of the reacting gas having the higher ionization potential, and retarded by addition of the gas with the lower potential. To illustrate: in the oxidation of hydrogen the rate for $2H_2-O_2$ mixture is 6.5 molecules per electron of current, in an $8H_2-O_2$ mixture it is 8.0 molecules per electron, while in an H_2-2O_2 mixture it is only 3.5 molecules per electron.

Additions of foreign gases to combining mixtures, with the exception of helium, retard the rate in proportion to the extent to which they absorb energy. Helium, with its high ionization potential of 24.5 volts, accelerates the rate up to

a partial pressure of about 50 per cent. The general conclusion may be drawn, therefore, that ions of the reacting gas having the lower ionization potential and ions of inert gases, except helium, are relatively ineffectual in initiating reactivity.

In decompositions the addition of foreign gases may or may not retard the rate, depending on the specific nature of the reaction. In the decomposition of nitrous oxide the rate is decreased by foreign gases to the extent to which they reduce the number of N_2O^+ ions as computed from the relative stopping power for electrons. The decomposition of nitrogen dioxide, on the other hand, is actuated by foreign ions almost as readily as by NO_2^+ ions.

Comparative Ion Efficiency. Since the length of the negative glow is exactly equal to the range of electrons for corresponding voltages as given by Lehmann, it seems justifiable to use Lehmann's values for the number of electron volts required to produce an ion pair, in computing the number of positive ions formed per electron in the negative glow. In making the calculations the positive ion current to the cathode was neglected, since it represents only a small per cent of the total current.² In cases where the number of electron volts required to produce one ion pair has not been determined by Lehmann, 45 was used as an average value.

In syntheses the number of molecules formed is used in the calculations while in decompositions the number decomposed is considered. M refers to the number of the various molecules underlined. The M/N ratios are given in Table I for both the total number of ions and for those ions having the higher ionization potential.

It is interesting to note that the M/N ratios computed above compare favorably with the values obtained by Lind with α -rays.⁵ The conspicuous fact to observe is that the ratios are all small, and that in no instance is it necessary for the initial reaction center to collide with more than three molecules for the reaction to go to completion.

Propagation Reactions

The various factors which determine the reactivity in the discharge respond in an entirely different manner for propagation reactions from that described for initial reaction centers. Nevertheless, it is possible, by gradual changes in the experimental conditions, to follow the reaction from the initial zero-order type through various stages involving reaction chains until the ignition point is reached.

TABLE I
M/N ratios

Reaction	$\frac{M}{e}$	$\frac{M}{N_T}$	$\frac{M}{N_R}$	<i>T</i> (°C)
$N_2 + 3H_2 = \underline{2NH_3}$	0.82	$\frac{0.82}{8.0} = 0.1$	$\frac{M}{N_2^+} = \frac{0.82}{4.5} = 0.2$	-183
$\underline{NH_3} \rightarrow N_2 + 3H_2$	3.7	$\frac{3.7}{8.0} = 0.46$		+20
$N_2 + 2O_2 = \underline{2NO_2}$	0.92	$\frac{0.92}{7.8} = 0.12$	$\frac{M}{N_2^+} = \frac{0.92}{2.7} = 0.35$	-183
$\underline{2NO_2} \rightarrow N_2 + 2O_2$	20.0	$\frac{20}{13} = 1.55$		+170
	60.0	$\frac{60}{13} = 4.65$		+20
$\underline{2N_2O} \rightarrow 2N_2 + O_2$	14.0	$\frac{14}{7} = 2.0$		+22
	14.0	$\frac{14}{7} = 2.0$		+500
$2H_2 + O_2 = \underline{2H_2O}$	6.5	$\frac{6.5}{10} = 0.65$	$\frac{M}{H_2^+} = \frac{6.5}{5} = 1.3$	-183
$2CO + O_2 = \underline{2CO_2}$	6.5	$\frac{6.5}{9} = 0.72$	$\frac{M}{CO^+} = \frac{6.5}{6.0} = 1.1$	-183
$CH_4 + 2O_2 = \underline{CO_2 + 2H_2O}$	10.5	$\frac{10.5}{8.3} = 1.3$	$\frac{M}{CH^+} = \frac{10.5}{2.8} = 3.8$	-183
$\underline{2CH_4} \rightarrow C_2H_4 + 2H_2$	3.1	$\frac{3.1}{7.8} = 0.4$		-183

M in syntheses is the number of molecules formed; in decompositions the number decomposing.
N_T is the total number of positive ions formed per electron of current.
N_R is the number of positive ions of reactant having the higher ionization potential.
e denotes electrons of current in the outer circuit.

The Effect of Pressure, Current, and Temperature. The reactivity in the positive column for explosive mixtures exhibits a marked interdependence between pressure, current, and temperature. For each explosive mixture a combination of these three factors can be chosen below which the rate is of zero order, the reaction behaving exactly as that in nonexplosive mixtures. Above these particular conditions the rate increases nearly hyperbolically with pressure, more nearly exponentially with current, and moderately with temperature; in

the hydrogen-oxygen reaction a 300°C rise above room temperature increases the rate eightfold. Ignition occurs when the rate versus current, temperature, or pressure curve becomes asymptotic with the rate axis. Ignition can be induced in the positive column when the total expenditure of energy in this region is less than one two-hundredths of that being expended in the negative glow where the reaction is strictly zero order. The rapid increase in rate with current suggests that energy states formed in the discharge other

than those serving as initial reaction centers are involved in the chain mechanism. The positive temperature coefficient indicates that the reaction chains are favored by high thermal states in the gas. The pressure effect, as will be seen in the next paragraph, results largely from a retardation in the rate of diffusion of the various contributing energy centers out of the path of the reaction chain.

The Effect of Added Gases. The influence of added gases on the rate of reaction is in distinct contrast to that described for nonpropagating reactions. The addition of various gases accelerates the rate to the extent to which diffusion is retarded. This is illustrated in the hydrogen-oxygen case in which hydrogen, helium, a mixture of hydrogen and oxygen ($2\text{H}_2:\text{O}_2$), water vapor, argon, nitrogen, oxygen, and nitrous oxide enhance the rate, the effect increasing in the order named. These results indicate that high energy states are necessary for the maintenance of the reaction chains, or, conversely, that the chains will tend to break upon entering a region of normal energy density.

Mechanism of Reaction

The results that have just been described make it possible to draw certain general conclusions concerning the reaction processes involved in the glow discharge; these conclusions are independent of any specific mechanism of reaction.

1. The reaction is induced by initial reaction centers. These centers are some energy-rich molecular state, and not regions of high energy density.

2. The initial reaction centers are formed only by primary processes occurring in the discharge, presumably by direct electron impact.

3. Nonpropagating reactions occur when the reaction centers collide with normal molecules. Energy over and above that contained in the initial centers is unnecessary for the reaction.

4. Propagation occurs in explosive mixtures when the initial reaction centers, or these centers associated with normal molecules, collide with energy-rich molecular states.

5. Processes which retard diffusion tend to enhance the effect of propagation, and to lower the energy input necessary for ignition.

Any detailed mechanism that may be suggested for the processes involved in the reaction about the active centers entails considerable speculation; in consequence an attempt to outline such a mechanism must be considered merely as a

working hypothesis. It is definite, however, that any tenable mechanism must conform to the observed facts outlined above.

There is considerable evidence to suggest that the primary reaction centers are positive ions formed by direct electron impact in the discharge. The fact that the temperature coefficient is zero or negative for nonpropagating reactions argues against the initial centers being atoms or excited molecules, since photochemical reactions which have been assigned to these states usually possess a positive temperature coefficient. Insofar as data are available the results indicate that the negative temperature coefficient for the rate can be correlated with the temperature coefficient for the dielectric constant of the gases present. Since the forces involved in the association of neutral molecules about an ion have been shown by Loeb⁶ to be a direct function of the dielectric constant of the molecules, the apparent relationship between temperature and dielectric constant suggests some type of cluster mechanism.

The fact that propagation occurs in the positive column but not in the negative glow may result from one of two possibilities: Either some active state is formed in the positive column and not in the negative glow which gives rise to reaction chains, or else some condition exists in the negative glow and not in the positive column which is detrimental to chain formation. While the data are insufficient to determine which of these two possibilities is correct, it seems very doubtful that any active state can be produced in the positive column that is not formed in greater abundance in the negative glow. The zero-order conditions prevailing in the negative glow suggest that the life of the active centers in the gas phase is too short to permit the development of reaction chains.

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THE MECHANISM OF IGNITION BY ELECTRIC DISCHARGES

B. W. BRADFORD AND G. I. FINCH

Imperial College of Science and Technology, South Kensington, London, England

The precise sequence of events by which a potentially explosive gaseous mixture is caused to ignite has for long been a matter of specification and experiment, and has suffered several reinterpretations in the light of various theories. Of the two commonest modes of ignition, electrical and thermal, the former, being inherently the more complex, has received the less attention. Its very complexity, however, insofar as it places a greater number of controllable variables at the disposal of the investigator, gives it added utility as a means of probing the molecular processes involved. This paper is intended briefly to survey the development of the theory of electrical ignition of explosive gaseous mixtures, and to give an account of its present position.

The general characteristics of electrical ignition can be briefly summarized: (1) *Limits of inflammability*. All combustible gases in admixture with air or oxygen have the property in common that explosion will only occur within certain limits of composition. In all cases which have been examined, more electrical energy is necessary to bring about ignition of mixtures near the limits than in the middle zone of the region of inflammability. In this respect electrical ignition differs markedly from thermal ignition. (2) *Limiting igniting pressure*. A given gaseous mixture becomes increasingly more difficult to ignite as its pressure is reduced, and a greater dissipation of electrical energy becomes necessary to initiate explosion. Hence the incendivities of different sparks may be compared by determining the least pressures at which they will ignite a given mixture. Such limiting pressures have only relative significance; up to the present time no absolute lower pressure limit for electrical ignition has been established. (3) *Least igniting energy*. Alternatively, the relative ignitabilities of different gas mixtures may be compared by measuring the least sparks which will ignite them. The igniting spark may be characterized, for example, by its total energy.

A bibliography of published work is appended to this paper. Because of imperfect control of electrical factors, much of the earlier work on electrical ignition cannot be used as a sound basis for generalization; indeed, progress has to a large extent been conditioned by improved control and understanding of the electrical factors underlying the phenomena. The development of early ideas may be briefly outlined.

The alternative possibilities that ignition might be the result either of specifically electrical effects or of thermal effects due to the conversion

of electrical energy to heat energy have been recognized from the time of the first systematic work on the subject. Coward and his collaborators^{8,9} determined the sensitivities of various gaseous mixtures by the method of limiting igniting pressures. Certain diluents (e.g., oxygen up to 70 per cent) were found to decrease the limiting (to certain arbitrary spark conditions) igniting pressures of hydrogen-oxygen mixtures, whilst others brought about an increase; a partial correlation appeared to exist between ignitability and thermal conductivity. Hence the view was taken that thermal factors were predominant, although it was necessary to make an exception in the case of carbon monoxide-oxygen mixtures, in which some specific activation of oxygen was suspected; the balance of evidence failed to decide whether thermal or electrical factors predominated. Similar phenomena have more recently received a different explanation based on chain propagation⁴⁴. It must, however, be pointed out in this connection that unless electrical factors are fully under control, data based on limiting igniting pressures may be misleading, since the electrical characteristics of a gaseous mixture can be, and often are, fundamentally altered by the addition of a diluent gas.

The first experiments in which systematic control of electrical conditions was aimed at were made by Thornton,^{45-50,63,51-55} using the method of least igniting energy or current. His work included studies of many different types of igniting agent, and led to the fundamentally important observation that a given amount of electrical energy can possess vastly different igniting powers when dissipated in different forms. For example, a capacity spark was found to be considerably more effective in igniting certain gases than a spark produced by breaking a circuit containing inductance, and the incendivity of the latter type of discharge increased as the voltage applied to the circuit increased. From the undoubted specificity of the discharge characteristics which Thornton's work revealed, he concluded⁴⁶ that ionization was the effective cause of ignition. More recently, however, in the light of the results to be described later, which led to the excitation theory of ignition, Thornton has recognized that ionization is not the only factor to be considered.⁴⁸

The Thermal Theory of Electrical Ignition

The question was reopened by Morgan²⁹. It has long been known that a spark discharge pro-

duced by an oscillation transformer, i.e., a coil or magneto, was a complex phenomenon consisting in the main of two characteristically different parts. One such part is due to the discharge, on breakdown of the gap, of the energy stored in the distributed self-capacity of the secondary circuit, and is termed the "capacity component." The subsequent discharge of electromagnetic energy through the secondary circuit forms what is known as the "inductance component" of the discharge. Morgan found that if a magneto is shunted by a variable air condenser, the incendivity of the spark so produced towards a particular gaseous mixture increased with increasing capacity. He concluded that the igniting power of an induction coil or magneto spark is associated chiefly with the capacity component, and only secondarily with the inductance component which follows it. Meanwhile Wheeler⁵⁹ had independently postulated that the necessary condition for ignition was that sufficient energy should be introduced to maintain for a sufficient time a sufficient volume of a gaseous mixture at or above its ignition temperature. Although experiments, designed to show whether incendivity could be correlated with the thermal properties of the gaseous mixture concerned or with its speed of flame propagation, yielded negative results,^{59,60} Wheeler found in the assumed general superiority of the capacity component in ignition a confirmation of a purely thermal view of electrical ignition phenomena, and jointly with Morgan and Taylor-Jones⁴³ put forward a thermal theory of ignition, ultimately depending on that assumption.

The theory was founded on analysis of the temperature distribution in a gas in the immediate neighborhood of various types of localized heat sources. Such analysis indicated that for a given amount of energy, an instantaneous point source was superior to a continued source and that a volume source was superior to a point source, and it was considered that these differences were sufficient to account for the marked effect which the precise mode of dissipation of given amount of electrical energy had on its igniting power—as shown by the researches of Thornton and others—without reference to ionization or any other specific characteristic of the spark discharge.

The theory was put by Morgan in the form "the ignition of a gaseous mixture depends primarily . . . on the raising of a sufficient volume to a sufficient temperature,"⁴³ with the corollary that "the heat energy required in the source to produce ignition is least when the heat is imparted instantaneously. When the rate of heat supply is less, a greater quantity of heat must be given to the gas before ignition can occur".³¹ The

theory was applied to various ignition phenomena (see Morgan,^{30-32,34,35} Morgan and Wheeler,³⁶ Coward and Meiter,¹⁰ Taylor-Jones,⁴² and Holm²⁴), nevertheless it embodied a principle which was inherently improbable. Taking the statement of the thermal theory as set forth above, it is not difficult to show that it implies the view that the igniting power of a given quantity of energy lies dormant until the energy is converted into heat and thus increases with increasing lack of availability of such source energy. For temperature, a statistical measure of the mean kinetic energy of the random translational motions of the molecules of a system, is a fundamental conception which loses in significance as the entropy falls below the maximum consistent with the energy of the system. As in the case of a single molecule, the term "temperature" is meaningless when applied to mass motion. And since, according to the thermal theory, ignition calls for the raising of the gas to a sufficient temperature, it is clear that this view suggests that in the case of a source of least igniting energy the entropy/energy ratio of the system must be at a maximum before ignition can be determined therein. Coward and Meiter,¹⁰ as a result of their experiments, appear indeed to have arrived at this conclusion, because they state that "nothing in the results of (their) experiments suggests the intervention of any electrical effect of the spark . . . other than the normal effect of the degradation of its electrical energy."

Characteristics of Gaseous Combustion in Electric Discharges

About this time there came to light a set of facts relating to gaseous combustion in electric discharges which put the question of spark ignition in a new light, and enabled it to be divorced from the older standpoint of thermal ignition with which it had hitherto been linked. These facts will be briefly reviewed.

A discharge between solid electrodes may take the form of either a low- or a high-tension arc, the essential difference being in the temperature of the cathode. The discharges employed in ignition are almost without exception of the high-tension type, and it has been shown by Finch and Cowen¹⁴ that a high-tension arc dissipating energy at a surprisingly high rate can be maintained in an explosive gaseous mixture without causing ignition. In such a discharge, three luminous zones are ordinarily distinguishable: (i) the cathode and negative glows sheathing the cathode and constituting the cathode glow, (ii) the anode glow or spot, and, finally, (iii) the positive column between which and the cathode zone lies the Faraday dark space. The positive

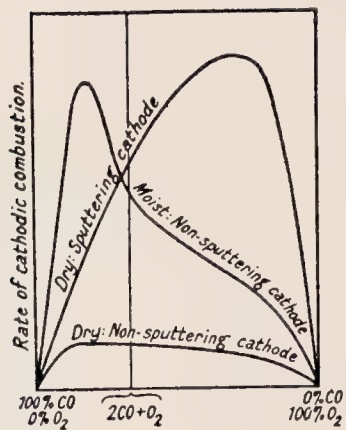


FIG. 1. Showing the change in rate of cathodic combustion with composition in moist and dry carbon monoxide-oxygen mixtures at sputtering and nonsputtering cathodes.

column can be wholly suppressed or varied in extent by a suitable choice of gap width, gas pressure, or current. Reduction of the positive column of a high-tension arc, maintained in an explosive mixture such as $2\text{H}_2 + \text{O}_2$, by decreasing the distance between the electrodes, in no way affects either the anode or the cathode glow, but proportionately reduces the rate of combustion¹⁴. Therefore some combustion occurs in the positive column; once the positive column has been eliminated, a further reduction in gap width merely encroaches on the Faraday dark space, but has no effect on the rate of combustion. It follows that combustion must be limited to the luminous zones of the discharge.

The rate of combustion in a discharge from which the positive column is absent is directly proportional to the current and independent of the nature of the anode material, but is profoundly affected by that of the cathode^{14,16}. For example, dry $2\text{CO} + \text{O}_2$ burns more than three

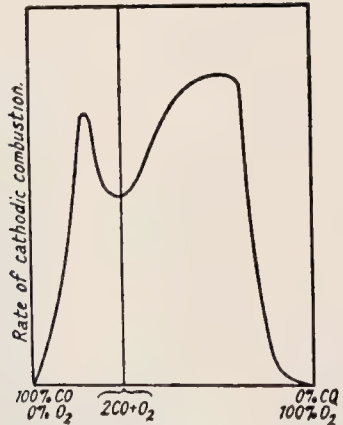


FIG. 2. Showing the change in rate of cathodic combustion with composition in moist carbon monoxide-oxygen mixtures at a sputtering cathode.

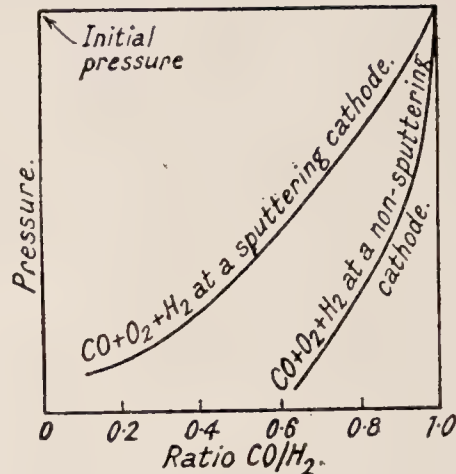


FIG. 3. Preferential combustion of carbon monoxide in a carbon monoxide-oxygen-hydrogen mixture.

times more rapidly at a silver cathode than at a copper cathode. It has been shown that this remarkable effect cannot be due to a difference in the cathode potential falls of different metals; it may therefore be concluded that in the absence of a positive column, combustion is confined to the cathode zone.

In suitable conditions the cathode potential fall is independent of either the current or the gas pressure; thus the rate of combustion is directly

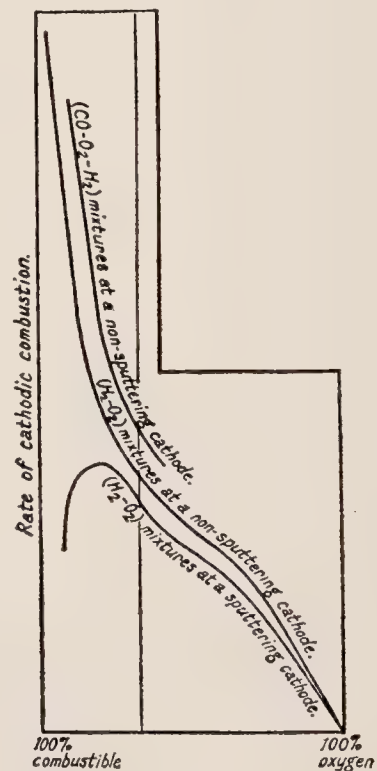


FIG. 4. Cathodic combustion of hydrogen-oxygen and carbon monoxide-oxygen-hydrogen mixtures. Rate of combustion to same scale as in Figs. 1 and 2.

related to the energy dissipated in the cathode zone. It has been established that the specific and very considerable influence which the nature of the cathode material exerts on the rate of cathodic combustion is not connected with the occurrence of heterogeneous combustion, as might at first sight be supposed, but that the effects are due to the influence of sputtered metal atoms, i.e., atoms of the cathode material torn from its surface and projected into the cathode zone under the influence of ionic bombardment.

Figures 1 to 4 summarize some of the results of a series of researches, for details of which reference must be made to the original papers.^{13-16,19} In these graphs the ordinates represent rates of cathodic combustion, expressed in terms of the ratio of the rate of combustion of the gas to the current carried by the discharge. Figures 1, 2, and 4 are drawn to the same scale.

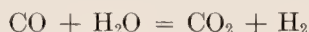
Dry $2\text{CO} + \text{O}_2$ burns slowly at a tantalum or tungsten, i.e., nonsputtering, cathode (Fig. 1), but at a freely sputtering cathode such as silver or gold, the metal atoms projected into the cathode zone effect an approximately fivefold increase in the rate of combustion, and a rather similar acceleration is brought about by the addition of water vapor (see Fig. 1).¹⁶ The accelerating effects of steam and of metal atoms are not, however, additive, for the presence of moisture slightly reduces the rate of combustion of a $2\text{CO} + \text{O}_2$ mixture at a sputtering cathode.¹⁹ Furthermore, the roles played by steam and by metal atoms in overcoming the reluctance of carbon monoxide to burn cathodically must differ fundamentally, because steam is most active in promoting the combustion of mixtures rich in carbon monoxide, whereas the rate of combustion of carbon monoxide at a freely sputtering cathode attains a maximum when excess oxygen is present (Fig. 1),¹⁹ while replacement of the excess of oxygen by helium or argon mainly results in a dilution effect. Finally, the independent modes of activity of steam and metal atoms in promoting the combustion of carbon monoxide-oxygen mixtures is established by the results recorded graphically in Fig. 2; when both steam and metal particles are present, the curve showing the relation between rate of cathodic combustion and mixture composition exhibits two characteristic maxima, one due to moisture when carbon monoxide is in excess, and the other due to sputtered metal atoms in oxygen-rich mixtures.¹⁹ Thus, steam and metal atoms do not interfere with each other to any material extent in promoting the cathodic combustion of carbon monoxide-oxygen mixtures.

From this and other cognate data it was concluded that the process of the combustion of carbon monoxide in different conditions may be

represented as follows:

- (i) Dry carbon monoxide-oxygen mixtures in the absence of metal atoms:
 - (a) $2\text{CO} = \text{CO}_2 + \text{C}$, and
 - (b) C is burnt by oxygen.
- (ii) Dry carbon monoxide-oxygen mixtures in the presence of metal atoms:
 - (a) $\text{Me} + \text{oxygen} = \text{MeO}$, an unstable metal oxide, and
 - (b) $\text{CO} + \text{MeO} = \text{CO}_2 + \text{Me}$

- (iii) Moist carbon monoxide-oxygen mixtures:



Carbon monoxide-oxygen-hydrogen mixtures containing not more than sufficient oxygen for complete combustion burn at either sputtering or nonsputtering cathodes in such a manner that carbon dioxide is more rapidly formed than is steam (Fig. 3); thus the carbon monoxide appears to burn more rapidly than does the hydrogen. The rates of cathodic combustion occurring in such mixtures at nonsputtering cathodes have, however, little or nothing in common with those observed in the case of either moist or dry carbon monoxide-oxygen mixtures; carbon monoxide-oxygen-hydrogen mixtures burn in general not only much faster, but the manner in which the rate of combustion varies with increasing combustible contents also bears no resemblance to that observed in the case of dry or moist carbon monoxide-oxygen mixtures (Fig. 1). A close parallel exists, however, between the rates of cathodic combustion of carbon monoxide-oxygen-hydrogen and hydrogen-oxygen mixtures; in both, the rates of combustion at a nonsputtering cathode increase rapidly and in a similar manner with increasing combustible contents^{19,17,13} (Fig. 4). Furthermore, within the limits hitherto examined, a partial substitution of carbon monoxide by an equivalent amount of hydrogen has little or no effect on the rate of combustion of carbon monoxide-oxygen-hydrogen mixtures. In view of these facts, it is difficult to resist the conclusion that, during the combustion of carbon monoxide-oxygen-hydrogen mixtures at a sputtering cathode, the hydrogen burns first and at a rate which in effect determines that of the mixture as a whole, and that the apparent preferential combustion, i.e., the more rapid disappearance of carbon monoxide, is due to oxidation by some product, or products, of the combustion of hydrogen which is thereby returned to the mixture; and, further, since the rate at which carbon monoxide burns when undergoing such preferential combustion is much higher than that observed in the case of

dry carbon monoxide-oxygen mixtures, it follows that carbon monoxide is burnt far more readily by the product or products of the combustion of hydrogen than by oxygen.

Moreover, the extent to which carbon monoxide burns preferentially in carbon monoxide-oxygen-hydrogen mixtures is far greater when combustion proceeds at a sputtering cathode than otherwise (Fig. 3), although the total rate of combustion is greatly reduced, in some cases by as much as three times, by the presence of metal atoms.¹⁹ These facts strongly suggest (i) that carbon monoxide is burnt by at least two oxidation products of hydrogen, one of which is more highly oxygenated than the other, and thus, on reduction, leads to the return of less hydrogen to the burning mixture, and (ii) that metal atoms either prevent the formation of or decompose the oxygen-rich hydrogen combustion product, and in this manner not only increase the extent to which the carbon monoxide is burnt preferentially, but are also responsible for the reduction in the rate of combustion in carbon monoxide-oxygen-hydrogen mixtures observed at a sputtering cathode. This view is further supported by the fact that hydrogen-oxygen and carbon monoxide-oxygen-hydrogen mixtures containing combustible in sufficient excess all burn at a sputtering cathode at a practically similar rate, which is, within wide limits, independent of the composition of the mixture.^{19,17}

In addition to steam, the chief oxidation products of hydrogen known to be formed within the cathode zone maintained in either steam or hydrogen-oxygen mixtures are hydroxyl, and possibly hydrogen peroxide, which has been detected, though only in small amounts, in the products issuing from the discharge.^{19,17} Hydrogen, however, is present in profusion.²²

It is improbable for several reasons that hydrogen peroxide plays any material role, and the facts strongly suggest that it is OH which, like steam, is so active in burning carbon monoxide, and that metal atoms neither decompose OH, nor do they prevent its formation from steam, but that sputtered metal in some manner inhibits the formation of OH as a direct intermediate product of the cathodic combustion of hydrogen to steam. Thus the combustion of carbon monoxide-oxygen-hydrogen mixtures at nonsputtering cathodes may be represented as follows:

- (a) H_2 burns *via* OH to H_2O ,
- (b) $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$, and
- (c) $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$

Oxygen-rich hydrogen-oxygen mixtures burn at relatively low rates at either a sputtering or a nonsputtering cathode. In the case of mixtures

containing excess hydrogen, however, and burning at a nonsputtering cathode, combustion increases at a remarkable rate with increasing hydrogen concentration, an effect which is almost wholly suppressed by the presence of metal atoms (Fig. 4).¹⁷ In the first place, these facts strongly suggest that both hydrogen and oxygen must be suitably excited before they can combine, and that the life of oxygen in the excited state is short, whilst that of the hydrogen is long. Further, the more than threefold reduction in the rate of cathodic combustion which can be and is effected by the presence of sputtered metal atoms can be reasonably explained, in accordance with the mechanism of the combustion of carbon monoxide-oxygen-hydrogen mixtures put forward above, as follows: Hydroxyl is an intermediate product in the normal combustion of hydrogen to steam. Metal atoms form with oxygen easily reduced oxides or unstable complexes which burn hydrogen to steam directly and thus suppress the intermediate formation of hydroxyl. Finally, since the rate of combustion of a hydrogen-rich hydrogen-oxygen mixture is much greater in the absence than otherwise of metal atoms, i.e., when OH is freely formed as an intermediate product, it may be concluded that OH in some manner powerfully promotes the combustion of hydrogen.

The fact that the rates of combustion of hydrogen-oxygen and of carbon monoxide-oxygen-hydrogen mixtures at a nonsputtering cathode increase rapidly and in a similar manner with increasing combustible contents (Fig. 4) suggests that the short life of oxygen in the suitably excited state for combustion with hydrogen is due to deactivation by collision with oxygen in some form or other, but not with hydrogen or carbon monoxide. Cool, arced, moist hydrogen contains much atomic hydrogen but reacts most reluctantly, if at all, with similarly arced oxygen, which is in a state of afterglow and rich in ozone undergoing decomposition¹²; thus the respective levels of excitation to which hydrogen and oxygen must be raised are high if they are to combine directly and without the intervention of any promotor of combustion such as OH. It is well known, however, that steam dissociates to a measurable extent at comparatively low temperatures of the order of 800°C. It follows that the energy required to bring about the decomposition of steam is far less than that necessary in order to excite hydrogen and oxygen sufficiently for them to combine directly. For thermochemical reasons, the most probable initial step in the mechanism of the decomposition of steam consists in the interaction of steam molecules, whereby hydroxyl and molecular hydrogen are formed.

Herein lies a probable explanation of the striking fact, discovered by Smithells, Whitaker, and Holmes⁴⁰ that the ignitability of a $2\text{CO} + \text{O}_2 + \text{H}_2$ mixture by a spark is greatly increased by a trace of steam. Thus, according to this view, a comparatively powerful discharge is required to ignite the rigidly dried mixture, because the initial formation of OH calls for the prior excitation of hydrogen and oxygen molecules to relatively high levels; in the case of the incompletely dried mixture, however, a much milder discharge suffices to produce hydroxyl by the decomposition of steam and thus to initiate combustion.

Concluding the summarized combustion mechanisms so far established: (i) hydrogen-oxygen mixtures in the absence of metal atoms: when the mixture is rigidly dried the initial step is (a) $\text{H}_2 + \text{O}_2 = 2\text{OH}$, but (b) $2\text{H}_2\text{O} = 2\text{OH} + \text{H}_2$ when moisture is present; whereupon OH in some manner acts as a powerful promotor in the succeeding stages of combustion. (ii) Hydrogen-oxygen mixtures in the presence of metal atoms: $\text{Me} + \text{oxygen} = \text{MeO}$, and $\text{H}_2 + \text{MeO} = \text{H}_2\text{O} + \text{Me}$.

These results provided clear evidence that the cathode zone of a high-tension discharge is a region in which gas molecules are excited to states of specific excitation which determine their subsequent reactivity, and that the gas in the path of the discharge is not merely heated by passage of the current.

Ignition by High-Tension, Direct-Current Discharges

At a given gas pressure, a high-tension, direct-current discharge can be maintained in an explosion gaseous mixture up to a limiting current; above this current the mixture explodes. The transition from steady combustion to ignition was the subject of a separate investigation¹⁴; in the case of $2\text{H}_2 + \text{O}_2$ mixtures it was shown, *inter alia*, that: (i) Ignition occurs without lag immediately on attainment of a certain limiting current; (ii) A hyperbolic relationship exists between the gas pressure and the igniting current over a considerable range of conditions; and (iii) A decrease in gap width, which results in a broadening out of the bright positive glow, increases the value of the igniting current.

On kinetic grounds, the concentration of ions, or of molecules or atoms excited to any particular state, is also approximately a hyperbolic function of gas pressure for conditions such as those under consideration, in which the potential drop across the discharge is constant. It follows, therefore, that in the conditions of these experiments, ignition was determined by the attainment of a

certain definite concentration of suitably excited molecules or atoms.

The Function of Ions

Ions, however, could not be excluded on the evidence so far available, although analyses of the rates of cathodic combustion of hydrogen and of carbon monoxide indicated that combustion was probably determined by excitation of the reactant molecules to states falling short of complete ionization. In the case of carbon monoxide a direct proof of this was furnished by a spectrographic examination.²² Spectrograms of the positive column and cathode zones of discharges at both sputtering and nonsputtering electrodes in carbon monoxide and in the mixture $2\text{CO} + \text{O}_2$ revealed the presence of carbon monoxide bands, but no evidence of ionized carbon monoxide. Carbon monoxide molecules in the discharge were therefore excited, but not ionized; hence it was clear, at least in the case of carbon monoxide, that combustion was determined by excitation falling short of ionization.

Excitation Theory of Electrical Ignition

From this and much other cognate evidence it became increasingly clear that the necessary prerequisite for the ignition of an explosive gaseous mixture was the setting up of a *sufficient concentration of suitably activated molecules*, and abundant indications existed that ignition by an electrical discharge depended on this specific activation and not on the fully degenerate activation associated with thermal energy, as postulated by the thermal theory of ignition. The two theories conflicted directly, and a crucial test between them was therefore devised.²³ The experimental method employed is shown in Fig. 5.

Mixtures of carbon monoxide and air in their equivalent proportions were ignited by means of condensed discharges of known oscillation frequency, and the igniting powers of the sparks were determined in terms of minimum igniting pressures, conditions being so arranged that the effect of frequency on igniting power could be studied independently of (i) the total amount of energy dissipated, or (ii) its rate of dissipation either during the first half-cycle or during the complete discharge.

The condenser was charged through a diode and discharged at a constant initial voltage of 8300 volts through a circuit containing a variable inductance but otherwise of negligible impedance. Hemispherical aluminum electrodes were used for the spark gap, this metal being chosen because of its low cathode potential fall and

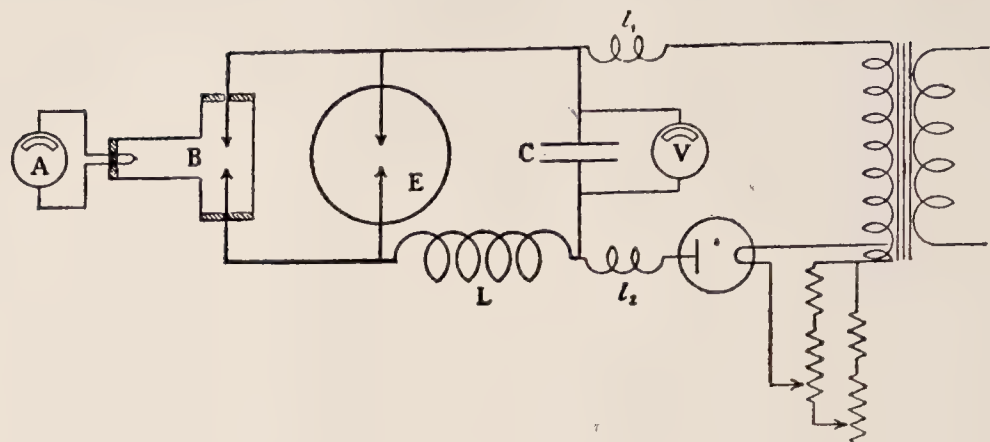


FIG. 5. Diagram of a condenser discharge circuit for ignition experiments (Finch and Thompson).

freedom from sputtering. A subsidiary spark gap discharging in a lagged chamber fitted with a thermocouple furnished a means of comparing the relative energies of different sparks. Experiments were carried out over a range of frequencies for a number of different capacities. The results are summarized in Fig. 6. It will be seen that for each value of the capacity the igniting power of the discharge increased with decreasing fre-

quency, in spite of the fact that the energy dissipated by the discharge decreased with decreasing frequency. Furthermore, it will be observed that the frequency of the discharge exerted a considerably greater effect on its igniting power than did its total energy. It is not difficult to see also that the igniting power of the spark was not determined by the value of the peak current. The experiments showed that the

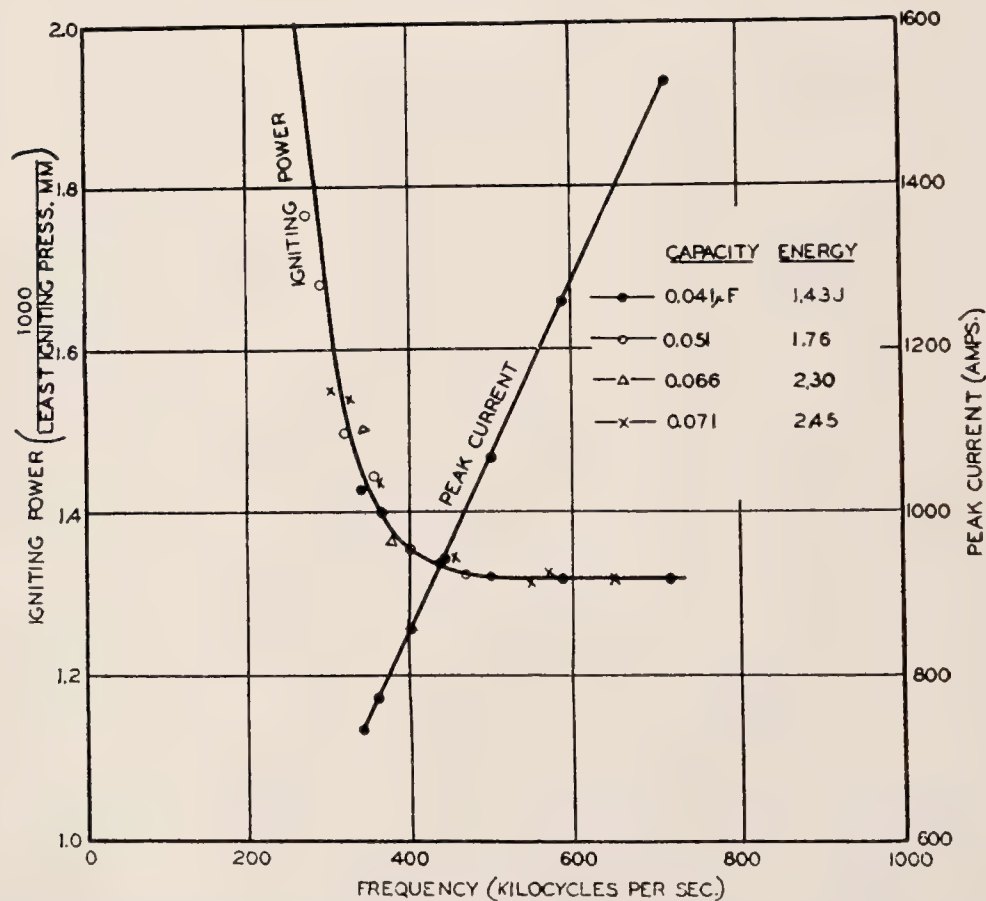


FIG. 6. Effect of frequency of discharge on its igniting power and on peak current. The peak current is for a capacity of 0.041 μ F; other capacities gave similar curves.

igniting power of a spark due to the discharge of a condenser through an inductive circuit is determined by the natural frequency of the circuit to such an extent that a suitable decrease in frequency may completely outweigh the effect of any possible reduction in igniting power due to either a decrease amount or rate of energy dissipation, or both, by either the first half-oscillation of a spark or by the entire discharge. According to the thermal theory, however, "ignition depends on the heating of a sufficient volume of the gas by conduction to a sufficient temperature",³⁴ which also implies that "the heat energy required in the source to produce ignition is least when the heat is imparted instantaneously. When the rate of heat supply is less, a greater quantity of heat must be given to the gas before ignition can occur".³¹ Hence it is clear that the conflict between the thermal theory and the facts set forth herein is complete. The mechanism of electric spark ignition, therefore, and indeed of ignition as a whole, cannot be adequately explained in terms of any purely thermal theory. On the other hand, the excitation hypothesis is consistent with and capable of explaining these facts. For, according to this view, ignition being primarily determined by the setting up of a sufficient concentration of suitably activated molecules, the imparting of energy to the molecules in such a manner as to bring about either an insufficient or excessive degree of activation is wasteful from the point of view of causing ignition. Now it is well known that the greater the frequency of a condensed discharge, the higher is the level to which the molecules are thereby activated. Thus the high-frequency spark is in general a rich source of ionization, whereas the low-frequency arc spectrum reveals mainly the presence of neutral atoms or molecules, and it may be concluded that in the present case a reduction in frequency resulted in an increase in the ratio between energy usefully expended in the production of suitably activated molecules and that otherwise dissipated.

Ignition by the Coil Discharge

There remained for solution the problem of the mechanism of ignition by a coil discharge, which is the case of practical importance. A systematic study of the phenomenon called for an investigation of the respective roles played by the two components of the coil discharge, and it was desirable to be able to modify or suppress one without materially affecting the other. Means of achieving this emerged from a consideration of the theory of the ignition coil based on a cathode-ray oscillographic study of the discharge.

Characteristics of the Ignition Coil Discharge

Neglecting the secondary resistance, the general coil circuit equations may be written:

$$L_1 di_1/dt + L_{12} di_2/dt + R_1 i_1 + e_1 = 0$$

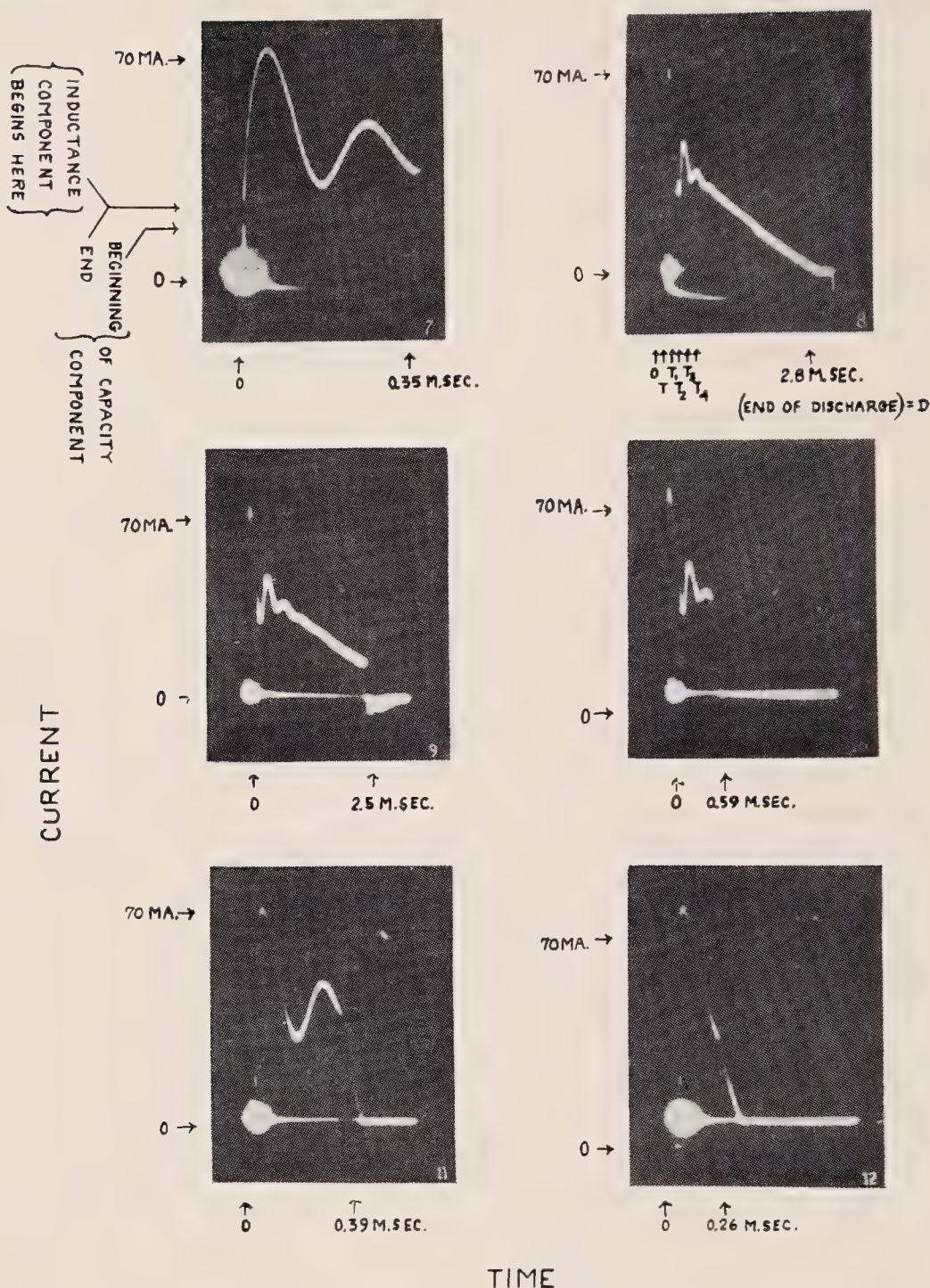
and

$$L_2 di_2/dt + L_{21} di_1/dt + e_2 = 0,$$

where L_1 , L_2 and C_1 , C_2 are the primary and secondary inductances and capacities respectively, R_1 is the primary resistance, i_1 and i_2 are the primary and secondary currents, e_1 and e_2 are the potential differences across the condensers, L_{12} and L_{21} are the coefficients of mutual induction of the secondary on the primary and of the primary on the secondary, respectively, and t is the time. Taylor-Jones⁴¹ has solved these equations for two special cases, i.e., (i) open-circuited secondary and (ii) secondary closed by an ohmic resistance, neither of which, however, is of much interest from the point of view of ignition, because, in the normal circumstances of its use, the coil is required to furnish a spark across a short fixed gap, the breakdown potential of which is much smaller than the maximum voltage which the coil is capable of exerting. The above equations can, however, be solved for the case of practical interest, provided the voltage-current characteristic of the spark be known.

Cathode-ray oscillographic analysis^{20,5} of a typical ignition coil discharge led to the following results. Upon breaking the primary circuit the discharge voltage rises in a manner determined by the coil constants and spark gap conductance to the breakdown potential of the gap, and then falls with extreme rapidity to a value at which it remains sensibly constant throughout the remaining life of the discharge. The corresponding current-time trace is shown completely in Fig. 8: the initial part of the current-time trace is best understood from Fig. 7, which was taken with a suitable air-dielectric capacity shunting the spark-gap. The gap in the trace near the origin corresponds to the discharge of the capacity component; the trace is invisible here because both the frequency and the amplitude of the discharge are exceedingly high. For a certain ignition coil assembly, for example, the frequency was of the order of 10^7 cycles, and the peak value of the current was calculated to be about 30 amp.

The spark potential is virtually constant and independent of the current during the life of the discharge; therefore no current flows in the secondary self-capacity during the discharge, and $L_{12} = L_{21}$. Hence it may be shown that in normal sparking conditions the inductance component rises to a maximum value of



FIGS. 7-12. Oscillograph records of induction coil spark discharges. FIG. 7, taken with a suitable air-dielectric capacity shunting the spark gap; FIG. 8, complete discharge; FIG. 9, late cut-off of discharge; FIG. 10, cut-off at T_3 ; FIG. 11, cut-off at T_2 ; FIG. 12, cut-off at T_1 .

$2i_0 \exp(-a\pi/2\alpha)$ and executes damped oscillations of initial amplitude ni_0 about a linear axis, the slope of which is given by $-e_2/L_2$. The total duration of the discharge is given by Mi_0/e_2 , where $M = L_{12} = L_{21}$.

Control of Spark Components

Thus the difference between the capacity and inductance components of the discharge is clear

and fundamental; their separation and control was carried out as follows: *The capacity component* can be practically eliminated by including in the secondary circuit a suitable diode run under such conditions as virtually to arrest the high currents of the capacity component whilst passing the inductance component unimpaired.⁵ In this manner the value of the capacity component may be reduced to the negligible quantity represented by the charging up of the gap interelectrode

capacity to the breakdown potential. *The inductance component:* Since the primary and secondary circuits in an ignition coil are closely coupled, the effective primary inductance must be small as long as the secondary is short-circuited by a spark. Hence if the primary circuit is closed during the life of the discharge, the primary current should build up exceedingly rapidly and since the energy would otherwise for the most part have appeared in the discharge, the latter would be expected to terminate abruptly. Analysis by means of the theory outlined above indicated that the spark should, in fact, terminate exceedingly abruptly, and a double interrupter¹¹ was designed which enabled the primary circuit to be remade at short and controllable intervals after break. The effect on the inductance component can be seen in the oscillograms (Figs. 7 to 12). Variation of the break-remake period, controlled by oscillographic observation, enabled the life of the inductance component to be varied from practically zero to its full value. The amplitude and frequency of the inductance component were controllable through the primary current and capacity.

Coil Ignition of Stagnant Gases

A series of critical experiments was planned to find whether the statement of Morgan and others (*loc. cit.*) that coil ignition is effected by the capacity and not by the inductance component is a justifiable generalization. The discharges employed were normal in every respect except that the life of the inductance component was varied as shown in Fig. 7 to 12. Table I shows a typical series of results with the explosive mixture $2\text{CO} + \text{O}_2 + 5\%\text{H}_2$.⁴ It was immediately clear that the igniting power of the spark decreased with progressive suppression of the inductance component, and when the least possi-

ble amount of inductance component energy was allowed to pass, the mixture failed to ignite at the highest pressure which could be employed without danger of shattering the explosion vessel. It may be emphasized that the capacity component was not reduced by progressive suppression of the inductance component, but must have increased for the igniting sparks; Paschen's law is known to hold with accuracy over the range of pressures employed, and the breakdown potential of the gap, and hence the energy of the capacity component, must therefore have increased with increasing gas pressure.

The same principle was shown to apply to ignition of the mixtures $2\text{H}_2 + \text{O}_2$ and $\text{CH}_4 + \text{O}_2$, but with the latter, cut-off of the inductance component had considerably less effect on the igniting power of the discharge. Thus, whilst a $2\text{CO} + \text{O}_2 + 5\%\text{H}_2$ mixture was relatively insensitive to ignition by the capacity component as compared with $\text{CH}_4 + 2\text{O}_2$, the position was reversed when the energy associated with the inductance component was increased to more than 10% of its maximum possible value.

It was clear therefore that the interaction of the spark and combustible gas molecules was complex and specific, and a study of the effects of further separation of the induction coil variables was necessary. As a final step, therefore, an investigation was made of the igniting powers of spark discharges modified in such ways as were necessary to isolate, not only the effect of the capacity component, but also the effects of the peak currents and duration of the inductance component.⁵ The discharge circuit conditions employed are shown in Table II.

With a normal inductance component duration the results were as shown in Table III.

Comparing the results for circuit conditions B and C(a) in the mixture $2\text{CO} + \text{O}_2 + 5\%\text{H}_2$ it will be seen that elimination of the capacity

TABLE I
Relation of coil ignition to inductance component

Cut-off (see Figs. 8 to 12)	Inductance component energy	Duration of inductance component	Igniting power = 1000/least igniting pressure	Least igniting pressure
	<i>mJ</i>	<i>msec</i>	<i>mm</i>	<i>mm</i>
End of discharge	20.5	2.81	9.43	106
<i>T</i> ₄	9.2	0.79	7.70	130
<i>T</i> ₃	7.4	0.59	7.41	149
<i>T</i> ₂	5.2	0.39	6.50	154
<i>T</i> ₁	2.4	0.20	5.13	195
<i>T</i>	<i>ca.</i> 0.15	0.02	4.26	235

TABLE II
Discharge circuit conditions employed

Circuit conditions	Nature of discharge	Current-time oscillogram
A. Unmodified.	Normal coil discharge	Fig. 8
B. Diode in series with gap shunted by condenser and filament fully heated.	Normal coil discharge	As in A
C. Diode without shunting condenser:		
(a) filament fully heated	Negligible capacity component; inductance component unimpaired	Fig. 14
(b) filament underrun	Negligible capacity component; normal (or nearly so) inductance component duration, but oscillations more or less damped out, according to extent of underrunning	Figs. 15 to 19.
D. Diode shunted by condenser; filament cold.	Normal capacity component; negligible inductance component.	
E. Diode as in D but without condenser.		

component of the discharge had an exceedingly small effect on its igniting power, and the mixture $\text{CH}_4 + \text{O}_2$ gave a similar result. The capacity component alone (circuit condition D) failed to ignite a $2\text{CO} + \text{O}_2 + 5\%\text{H}_2$ mixture at the highest pressure which could be safely employed; in $\text{CH}_4 + \text{O}_2$ ignition could be brought about by its sole agency, but at a greatly increased pressure.

The effect was even more striking when the inductance component energy was reduced by cutting off to a value nearer the capacity component energy. For example, with an inductance component duration of 0.38 msec (i.e., a duration nearly half that shown in Fig. 19) inductance component energy (without associated capacity component) amounting to 5.11 mJ ignited a $2\text{CO} + \text{O}_2 + 5\%\text{H}_2$ mixture at 152 mm, while

TABLE III
Results with a normal inductance component duration

Circuit conditions	Least igniting pressure, mm	Igniting power	Capacity component, mJ	Inductance component	
				Engery, mJ	Duration, msec
Mixture 2CO + O ₂ + 5%H ₂					
A	92.5	10.8	0.62	29.8	3.66
B	108.0	9.3	0.84		
C(a)	111.0	9.0	0.89		
D	No ignition at 304.0	3.3	6.7		
E	No ignition at 313.0	3.2	7.1		
Mixture CH ₄ + O ₂					
A	89.5	11.2	0.58	23.8	2.67
B	90.5	11.1	0.59		
C(a)	92.0	10.8	0.61		
D	224	4.5	3.6		
E	No ignition at 250	4.0	4.5		

capacity component energy of 8.8 mJ, without any succeeding inductance component energy, failed to ignite at a pressure of 350 mm; the behavior of methane was similar. These results not only bring out the relative inefficiency of a high-frequency oscillatory discharge as a source of ignition, but also enable the conclusion to be drawn that the igniting power of any subsequent inductance component is but little, if at all, enhanced by a preceding capacity component of dimensions similar to that met with in normal coil practice.

Variation of the inductance component energy, the peak current, and discharge life gave results which are summarized in Fig. 13. These again show clearly that the igniting power of the coil discharge is associated in the main with its inductance component, and, further, that not only the total energy of this component but also the peak and mean rates of dissipation of such energy influence the igniting power to extents which vary with the nature of the explosive mixture. For example, whilst in the case of all the mixtures an increase in either the peak rate of dissipation of energy or the total amount of energy resulted

in an increase of igniting power, the influence of the total duration of the discharge varied according to the nature of the gas mixture. Thus, prolongation of the discharge beyond the second inductance component oscillation failed to effect any pronounced increase in the igniting power in the case of the methane mixture, whereas with $2\text{H}_2 + \text{O}_2$, and even more so in the case of $2\text{CO} + \text{O}_2 + 5\%\text{H}_2$, the igniting power of the discharge increased steadily with increasing duration. With a damped and partially cut-off inductance component (as in Fig. 15 to 19) dissipating, e.g., 10 mJ, the order of decreasing sensitivity to ignition of the mixtures was $2\text{H}_2 + \text{O}_2$, $2\text{CO} + \text{O}_2 + 5\%\text{H}_2$, $\text{CH}_4 + \text{O}_2$; on the other hand, dissipation of a similar amount of energy in the form of a normal undamped, but suitably cut-off inductance component (as in Figs. 7 to 12) resulted in an inversion of this order (see Fig. 13), thus confirming the fact already brought out that whilst methane was more particularly sensitive to the peak rate of energy dissipation, the ignition of the other mixtures could be brought about more efficiently by increasing the life of the discharge at the expense of the peak rate of

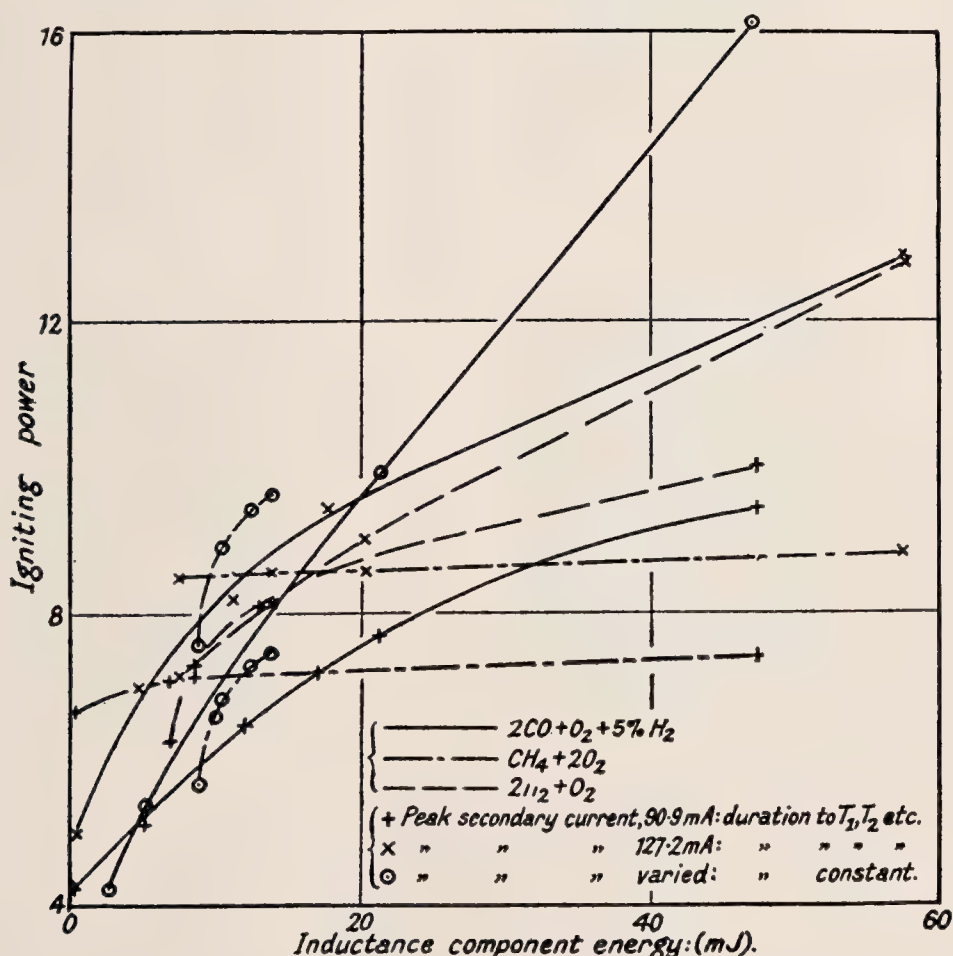
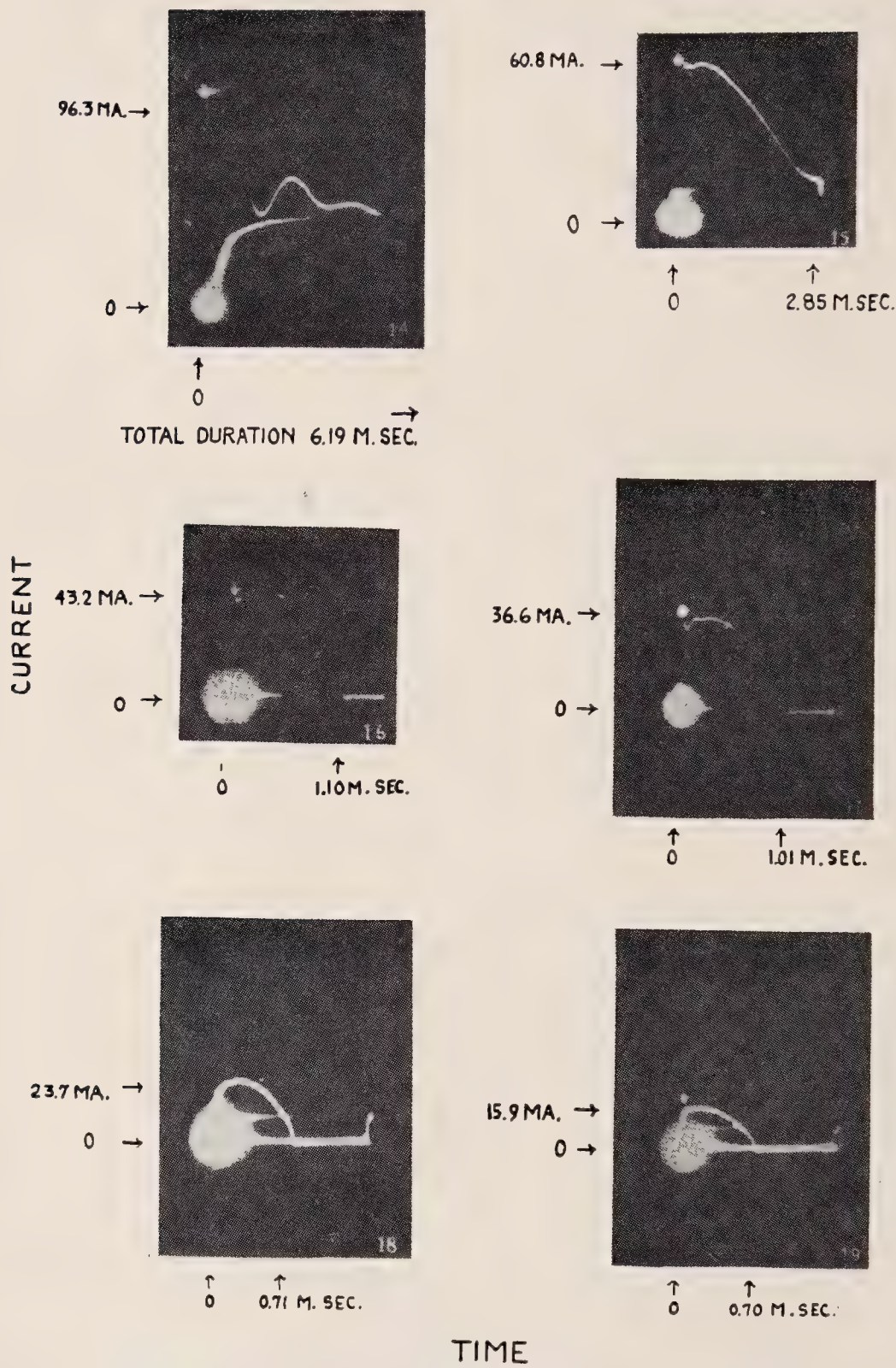


FIG. 13. Relation of igniting power of spark discharges to the energy in the inductance component for various gas mixtures



FIGS. 14-19. Oscillograph records of induction coil spark discharges

energy dissipation, the total spark energy remaining otherwise unchanged.

Spark Ignition in the Internal-Combustion Engine

In the case of the experiments so far discussed, the ignition pressures were of the order of 0.1 to 0.2 atm, and the gas was both cool and stagnant. In the engine, however, the gas pressure at the moment of ignition is of the order of 10 atm, the gas is hot as a result of preheating and adiabatic compression, and is furthermore in a highly turbulent state. In order to bring out the practical bearing of the results obtained with stagnant gases, further experiments in which account was taken of these important changes in conditions were carried out with a standard four-cylinder petrol engine¹⁸. For details, the original paper must be consulted; among the more important points established were the following: (i) Power output, efficiency, and speed were alike unaffected by cutting off the latter part of the inductance component, so that the total spark duration was reduced, in one case, for example, from 2.0 to 0.5 msec; (ii) Variation of peak secondary current in the inductance component was also without effect on the engine characteristics; and (iii) When the duration of the discharge was reduced sufficiently, misfiring occurred, and it was proved that the misfires were due to the occasional failure of the spark to jump the plug points, and not to the failure of the spark to ignite the explosive mixture. In the engine cylinder the conditions are so far removed from the limits that the igniting power of any spark furnished by the coil is greater than the least igniting value, and even if the spark consists only of the capacity component of the discharge, ignition occurs without fail.

The results proved that the only part of the ignition coil discharge required for ignition of the explosive mixture in an internal-combustion engine is the capacity component, the discharge of which can be insured in spite of a relatively high plug conductance by the retention of only a short initial portion of the inductance component, and the discharge duration can be reduced to one-tenth and possibly much less, without affecting either the igniting properties of the spark or the performance of the engine.

Conclusion

The researches which have been outlined above enable the view that electrical ignition is attributable to purely thermal effects of the spark to be dismissed. For not only has a large body of evidence been accumulated which shows that an

electrical discharge is a region in which gas molecules are activated directly to states in which they are capable of taking part in the process of combustion, but it has also been shown experimentally that electrical ignition does not possess the characteristics which a purely thermal process of ignition would require. The facts relating to the ignition of gases, so far as they are now known, are, however, consistent with the view that combustion is determined by a prior excitation of the molecules to suitable energy levels; excitation falling short of, or exceeding, such levels leads in the main to waste of igniting energy. According to this quite general "excitation" view of ignition, temperature, as a measure of collision frequency, is only of secondary significance. Heat is but one of several forms of energy capable of giving rise to suitable excitation and, owing to the random element, by no means necessarily the most efficient.

The further definition of the precise mechanism by which an electrical discharge initiates an explosion in any particular gaseous mixture must depend on a full exploration of that system. Sufficient has been outlined above to show that the combustible gases which have so far been examined, i.e., carbon monoxide, hydrogen, and methane, differ characteristically in their response to discharges of various types. No attempt will be made here to explain the possible causes of the specific influence of the combustible gas; work shortly to be published on the cathodic combustion of methane bears on this point. As an indication of the lines along which many of the phenomena of ignition may be quantitatively expressed in terms of the rates at which activation and deactivation occur in various types of discharge, a paper by Mole²⁵ may be consulted.

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THE IGNITION OF GASES BY LOCAL SOURCES

H. G. LANDAU

Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pennsylvania

When energy is released by a local source such as an electric spark in a combustible gaseous mixture, it is assumed to heat instantaneously a small volume and also to create active particles, chain carriers, which diffuse through the gas and increase in number by chain-branching processes at a rate proportional to their concentration. The heat-producing reaction proceeds at a rate proportional to concentration of active particles. Taking as a criterion for ignition the requirement that the temperature at the point of ignition shall never decrease, the following condition for ignition is obtained:

$$A = \frac{4(T_1 - T_0)k}{Qn_0R^2}$$

must be less than or equal to a value depending on α , the relation being given in Fig. 1.

The significance and applicability of this result are discussed.

Although the ignition of gases by local sources (mainly electric sparks) has been the subject of extended experimental investigations, there has been very little theoretical consideration of this topic. A paper by Taylor-Jones, Morgan, and Wheeler,⁷ one by Silver,⁶ and another by Mole² exhaust the list. At present the literature on ignition seems to consist mainly of an enormous collection of experimental data with insufficient theoretical basis to coordinate the data, to indicate the significance of experimental results, or to supply a ground for prediction. It was therefore felt that a theoretical study, even if only partially correct, might indicate lines of research that would help to eliminate the somewhat confused state of the literature on the subject.

Physical Assumptions

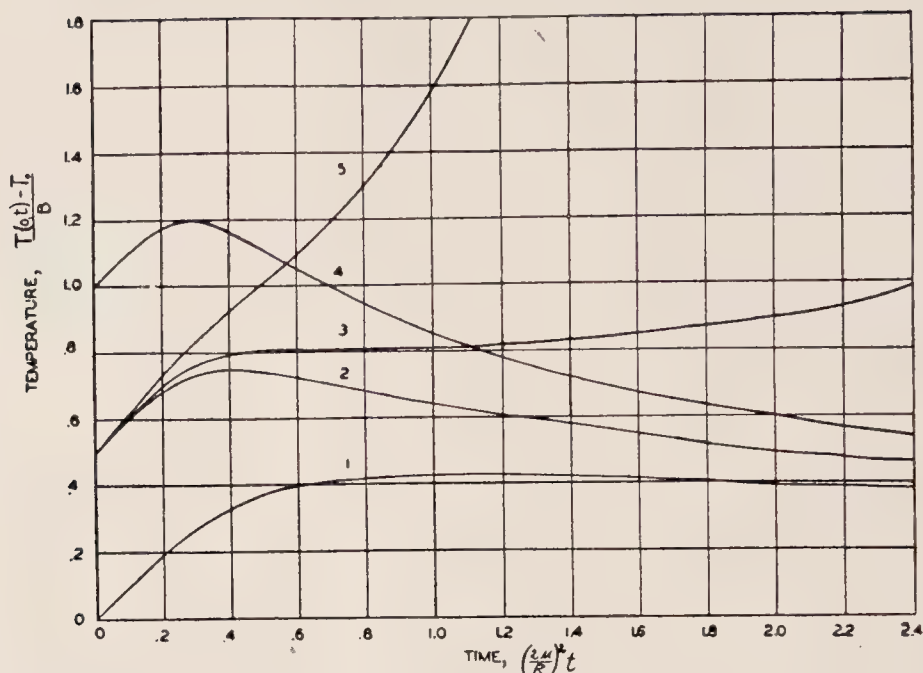
In order to treat the problem mathematically, it is necessary to adopt a definite physical mechanism for the process. We conceive of the problem of the ignition of gases as follows: In a combustible gaseous mixture contained in a large vessel there is an arrangement for rapidly releasing energy within a small volume at a distance from the walls, for example, by passing an electric spark. It is assumed that the energy instantaneously heats up a small spherical volume and creates active particles. These active particles are the chain carriers of the chain-reaction theory; it is not necessary to state whether they are ions, atoms, molecules with an excess of energy, or something else. It is also not necessary to specify the mechanism by which these active particles are created, but simply to assume that the release of energy does create them. The following processes then take place: There is a heat-generating reaction which is assumed to proceed at a rate proportional to the concentra-

tion of active particles, but this concentration varies with distance and time because the active particles are diffusing through the gas, and in addition are increasing in number at a rate proportional to their concentration; that is, chain branching is occurring. We are interested mainly in temperature, and so the chemical reaction enters the picture only insofar as it generates heat; it is not necessary to make any statements about the mechanism of the reaction except that it proceeds at a rate proportional to the concentration of active particles. Similarly, no particular mechanism for chain branching need be introduced.

Now the temperature at the center of the sphere tends to fall because of conduction of heat away from it, and to rise because of the heat generated. In some cases it rises continuously, and in others it shows a drop after a time (Fig. 1). Some criterion for ignition is needed, and the most natural one to use is the requirement that the temperature at the center of the sphere shall never fall. This can be justified by the fact that both the rate of the heat-generating reaction and of chain branching increase with increasing temperature, so that a temperature drop would slow them down, thus causing a further drop in temperature, and eventually making the reaction stop altogether.

In the following section the partial differential equations for the concentration of active particles and for temperature are stated and solved. Then the criterion for ignition is applied, giving a relation between the physical constants which must hold for ignition to take place.

It is assumed that the diffusion coefficient of the active particles is equal to the thermometric conductivity (thermal conductivity divided by specific heat per unit volume) of the gas through which they diffuse. If the active particles and the

FIG. 1. Temperature at the origin for various values of A and m

	A	m	
Curve 1:	0	0	No ignition
Curve 2:	0.5	0	No ignition
Curve 3:	0.5	0.64	Ignition, at limit
Curve 4:	1	0	No ignition
Curve 5:	0.5	1	Ignition

$$B = \frac{Qn_0R^2}{4k}$$

gas are the same molecular species, this is the result given by the elementary kinetic theory of gases.¹ This is not quite exact, but the difference is not serious; experimental values for the ratio of diffusion coefficient to thermometric conductivity lie between 0.7 and 1. It is not impossible to solve the equations without this assumption, but the result is not enough closer to physical reality to justify the greatly increased complications.

It is obvious that many factors have been omitted from the picture given above. The rates of the heat-generating reaction and of chain branching are not merely proportional to the concentration of active particles, but are also functions of temperature. The effects of changes in pressure and of the presence of burned gas have also been left out of consideration. However, an attempt is not being made to set up a mechanism for the complete course of the reaction. This discussion is concerned only with a condition for ignition, and since the question as to whether ignition takes place or not is decided within a very short time, it is reasonable to assume that

these omitted factors do not change very greatly within this time.

Solution of Equations

To make clear exactly what is involved, we restate in more general terms the problem which is treated here.

Consider a heat-conducting medium of infinite extent which is initially at temperature T_0 except within a sphere of radius R , where the initial temperature is T_1 . At the start this sphere is filled with active particles in the concentration n_0 per unit volume. These active particles diffuse through the medium; each generates Q units of heat in unit time and they increase in number at a rate proportional to their concentration. We wish to determine the relation that must exist among the physical constants for the temperature at the center of the sphere never to decrease.

The differential equation for the concentration of active particles is

$$\partial n / \partial t = \mu^2 \nabla^2 n + \alpha n \quad (1)$$

with the initial condition

$$\left. \begin{aligned} n &= n_0 & \text{for } 0 \leq r < R \\ n &= 0 & \text{for } r > R \end{aligned} \right\} \text{ when } t = 0, \quad (2)$$

where $n = n(r, t)$ is the concentration of active particles at a distance r and time t ; μ^2 = diffusion coefficient; ∇^2 = Laplacian differential operator, here

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right);$$

α = branching coefficient; and n_0 = initial concentration in the sphere of radius R . Equation (1) is merely the diffusion equation⁴ with the additional term αn giving the rate of increase of active particles.

To solve this put $n = e^{\alpha t} f(r, t)$. Then $f(r, t)$ satisfies the diffusion equation [that is, Eq. (1) without the branching term αn] and the same initial condition. This has the solution⁵

$$f(r, t) = n_0 U(r, t),$$

where

$$\begin{aligned} U(r, t) &= \frac{1}{2} \left[\operatorname{erf} \left(\frac{R+r}{2\mu\sqrt{t}} \right) + \operatorname{erf} \left(\frac{R-r}{2\mu\sqrt{t}} \right) \right] \\ &+ \frac{\mu}{r} \sqrt{\frac{t}{\pi}} \left[\exp - \left(\frac{R+r}{2\mu\sqrt{t}} \right)^2 - \exp - \left(\frac{R-r}{2\mu\sqrt{t}} \right)^2 \right] \end{aligned} \quad (3)$$

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-s^2) ds \quad (4)$$

being the error function or probability integral. Then

$$n(r, t) = n_0 e^{\alpha t} U(r, t) \quad (5)$$

is the solution of Eqs. (1) and (2).

Since the function $U(r, t)$ is to be used again, it is worth noting its meaning. As here introduced, $U(r, t)$ gives the concentration of diffusing particles in an infinite medium when the initial concentration is 1 within a sphere of radius R , and 0 outside this sphere. Since the heat conduction equation³ is of the same form as the diffusion equation, $U(r, t)$ also gives the temperature in an infinite medium due to an initial temperature of 1 within the sphere and of 0 outside.

$U(r, t)$ can also be regarded in a slightly different manner. Instead of considering an initial temperature distribution, consider an instantaneous spherical volume source of heat which generates enough heat to raise the temperature of the sphere from 0 to 1. If this generation of heat occurs at time $t = 0$, the tempera-

ture will be given by $U(r, t)$. If it occurs at time $t = \tau$, the temperature at any later time will be given by $U(r, t - \tau)$. These considerations will be used in finding the temperature distribution in the gas.

The partial differential equation for temperature is

$$\partial T / \partial t = \mu^2 \nabla^2 T + (Q/c) n(r, t) \quad (6)$$

with initial condition

$$\left. \begin{aligned} T &= T_1 & \text{for } 0 \leq r < R \\ T &= T_0 & \text{for } r > R \end{aligned} \right\} \text{ when } t = 0, \quad (7)$$

where $T = T(r, t)$ is the temperature at distance r and time t ; μ^2 = thermometric conductivity (the same symbol is used as for diffusion coefficient because these are assumed equal as explained above); Q = quantity of heat generated in unit time by the action of each active particle; c = specific heat of unit volume; T_1 = initial temperature of the sphere of radius R ; and T_0 = initial temperature outside this sphere.

Equation (6) is the heat conduction equation³ with the additional term $(Q/c)n(r, t)$, which gives the rate of temperature rise due to the heat produced by the action of the active particles.

This may be solved as follows. Put

$$T = T_0 + (T_1 - T_0) U(r, t) + V(r, t). \quad (8)$$

Then $T_0 + (T_1 - T_0) U(r, t)$ satisfies the heat conduction equation [that is, Eq. (6) without the term $(Q/c)n$] and the initial condition. $V(r, t)$ must then satisfy Eq. (6) and vanish everywhere when $t = 0$; it is the temperature due to a heat source generating $Qn(r, t)$ units of heat in unit time.

Now, as noted before, the temperature due to an initial distribution can be reinterpreted as that due to an instantaneous heat source. The temperature due to a spherically symmetric initial distribution, $\phi(r)$, is⁵

$$\frac{1}{2\mu r \sqrt{\pi t}} \int_{-\infty}^{\infty} \phi(\rho) \exp \left[- \left(\frac{\rho - r}{2\mu\sqrt{t}} \right)^2 \right] \rho d\rho^*$$

[with $\phi(-\rho)$ put equal to $\phi(\rho)$].

Then the temperature due to an instantaneous volume source which generates $Qn(r, t)$ units of heat at time $t = \tau$ is

$$\begin{aligned} W(r, t; \tau) &= \frac{1}{2\mu r [\pi(t - \tau)]^{\frac{1}{2}}} \\ &\times \int_{-\infty}^{\infty} \frac{Q}{c} n(\rho, \tau) \exp \left[- \left(\frac{\rho - r}{2\mu(t - \tau)^{\frac{1}{2}}} \right)^2 \right] \rho d\rho. \end{aligned} \quad (9)$$

* $U(r, t)$ is, of course, obtained by putting

$$\begin{aligned} \phi(\rho) &= 1 & \text{for } -1 < \rho < 1 \\ \phi(\rho) &= 0 & \text{elsewhere.} \end{aligned}$$

Since $W(r, t; \tau)$ is the temperature at r and t due to a source at time τ , the temperature due to the continuous source $Qn(r, t)$ can be obtained by integrating $W(r, t; \tau)$ for $\tau = 0$ to $\tau = t$. Thus,

$$V(r, t) = \int_0^t W(r, t; \tau) d\tau \quad (10)$$

The reasoning by which this result has been obtained has been more physical than mathematical. A more rigorous proof of the fact that $V(r, t)$ satisfies Eq. (6) can be given along the following lines. First note that $W(r, t; \tau)$ satisfies

$$\partial W / \partial t = \mu^2 \nabla^2 W \quad (11)$$

for all $\tau < t$, as can be shown by direct calculation. Then

$$\frac{\partial V}{\partial t} = \int_0^t \frac{\partial W}{\partial t} d\tau + \lim_{\tau \rightarrow t} W(r, t; \tau). \quad (12)$$

It can be shown that

$$\lim_{\tau \rightarrow t} W(r, t; \tau) = (Q/c)n(r, t) \quad (13)$$

as follows: Put $\rho = r + 2\mu(t - \tau)^{1/2}\lambda$ and substitute in Eq. (9); then

$$\begin{aligned} W(r, t; \tau) &= \frac{1}{r\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{Q}{c} n(r + 2\mu(t - \tau)^{1/2}\lambda, \tau) \\ &\quad \times \exp(-\lambda^2) [r + 2\mu(t - \tau)^{1/2}\lambda] d\lambda \\ &= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{Q}{c} n(r + 2\mu(t - \tau)^{1/2}\lambda, \tau) \\ &\quad \times \exp(-\lambda^2) d\lambda + \frac{2\mu(t - \tau)^{1/2}}{r\sqrt{\pi}} \\ &\quad \times \int_{-\infty}^{\infty} \frac{Q}{c} n[r + 2\mu(t - \tau)^{1/2}\lambda, \tau] \cdot \exp(-\lambda^2) \lambda d\lambda \end{aligned}$$

Putting $\tau = t$, the second integral vanishes and the first is

$$\frac{Qn(r, t)}{c} \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp(-\lambda^2) d\lambda = \frac{Qn(r, t)}{c},$$

giving Eq. (13). Then,

$$\begin{aligned} \mu^2 \nabla^2 V(r, t) &= \mu^2 \int_0^t \nabla^2 W(r, t; \tau) d\tau \\ &= \mu^2 \int_0^t \frac{\partial W}{\partial t} d\tau \end{aligned} \quad (14)$$

from Eq. (11).

From Eqs. (12)–(14), it follows that

$$\partial V / \partial t = \mu^2 \nabla^2 V + (Q/c)n(r, t),$$

showing that $V(r, t)$ satisfies Eq. (6).

Substituting the value of $n(r, t)$ from Eq. (5)

in Eq. (9) and carrying out the integration† there results

$$W(r, t; \tau) = \frac{Qn_0 e^{\alpha r}}{c} U(r, t). \quad (15)$$

It is worth noting the physical reason for this simple result. $U(r, t)$ is the temperature distribution due to an instantaneous spherical volume source at $t = 0$. Since our source,

$$(Q/c)n(\rho, \tau) = (Qn_0/c)e^{\alpha r}U(\rho, \tau)$$

has the value of U at time τ (except for the factor $e^{\alpha r}$), it follows that it will have the same value as U at any later time.

From Eq. (10) there results

$$V(r, t) = \frac{Qn_0}{c} \frac{e^{\alpha t} - 1}{\alpha} U(r, t) \quad (16)$$

† The following definite integrals are involved

$$\begin{aligned} \int_{-\infty}^{\infty} \operatorname{erf}(a + bx) \exp(-x^2) dx &= \sqrt{\pi} \operatorname{erf}\left(\frac{a}{(1 + b^2)^{1/2}}\right) \\ \int_{-\infty}^{\infty} \operatorname{erf}(a + bx)x \exp(-x^2) dx &= \frac{b \exp[-a^2/(1 + b^2)]^{1/2}}{(1 + b^2)^{1/2}}. \end{aligned}$$

These can be established as follows: Let

$$I(a, b) = \int_{-\infty}^{\infty} \operatorname{erf}(a + bx) \exp(-x^2) dx$$

$$\frac{\partial I}{\partial a} = \frac{2}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp[-(a + bx)^2 - x^2] dx$$

$$= \frac{2}{\sqrt{\pi}} \exp[-a^2/(1 + b^2)] \int_{-\infty}^{\infty}$$

$$\times \exp\left[-\left[(1 + b^2)^{1/2}x + \frac{ab}{(1 + b^2)^{1/2}}\right]^2\right] dx$$

$$= \frac{2}{(1 + b^2)^{1/2}} \exp[-a^2/(1 + b^2)].$$

Then,

$$I(a, b) = \sqrt{\pi} \operatorname{erf}\left(\frac{a}{(1 + b^2)^{1/2}}\right) + f(b)$$

but $I(0, b) = 0$, since

$$\int_{-\infty}^a \operatorname{erf}(bx) \exp(-x^2) dx$$

$$= -\int_0^{\infty} \operatorname{erf}(bx) \exp(-x^2) dx$$

so that $f(b) = 0$. Similarly for the other integral.

and finally, from Eq. (8)

$$T(r, t) = T_0 + \left(T_1 - T_0 + \frac{Qn_0}{c} \frac{e^{\alpha t} - 1}{\alpha} \right) U(r, t), \quad (17)$$

giving the desired temperature distribution.

Condition for Ignition

To obtain the condition for ignition, consider the temperature at the origin

$$T(0, t) = T_0 + \left(T_1 - T_0 + \frac{Qn_0}{c} \frac{e^{\alpha t} - 1}{\alpha} \right) \times \left[\operatorname{erf} \frac{R}{2\mu\sqrt{t}} - \frac{R}{\mu(\pi t)^{1/2}} \exp \left(-\frac{R^2}{4\mu^2 t} \right) \right]. \quad (18)$$

This changes with time at the rate

$$\begin{aligned} \frac{\partial T(0, t)}{\partial t} = & - \left(T_1 - T_0 + \frac{Qn_0}{c} \frac{e^{\alpha t} - 1}{\alpha} \right) \\ & \times \frac{R^3}{4\sqrt{\pi}\mu^3 t^{5/2}} \exp \left(-\frac{R^2}{4\mu^2 t} \right) \\ & + \frac{Qn_0}{c} e^{\alpha t} \left[\operatorname{erf} \frac{R}{2\mu\sqrt{t}} - \frac{R}{\mu(\pi t)^{1/2}} \exp \left(-\frac{R^2}{4\mu^2 t} \right) \right]. \end{aligned} \quad (19)$$

To determine the relation which holds between the physical constants when

$$\frac{\partial T(0, t)}{\partial t} \geq 0$$

put

$$x = R/2\mu\sqrt{t}$$

$$\alpha = m(2\mu/R)^2$$

$$A = \frac{4(T_1 - T_0)k}{Qn_0 R^2} \quad (k = \text{thermal conductivity} = \mu^2 c),$$

then,

$$\begin{aligned} \frac{\partial T(0, t)}{\partial t} = & \frac{2Qn_0}{c} x^5 \exp(-x^2) \\ & \times \left[-A - \frac{\exp(m/x^2) - 1}{m} + \frac{\exp[(m/x^2) + x^2]}{x^5} \right. \\ & \left. \times \left(\frac{\sqrt{\pi}}{2} \operatorname{erf} x - x \exp(-x^2) \right) \right]. \end{aligned} \quad (20)$$

The function

$$\begin{aligned} F(x) = & \frac{\exp[(m/x^2) + x^2]}{x^5} \\ & \times \left(\frac{\sqrt{\pi}}{2} \operatorname{erf} x - x \exp(-x^2) \right) - \frac{\exp(m/x^2) - 1}{m} \end{aligned}$$

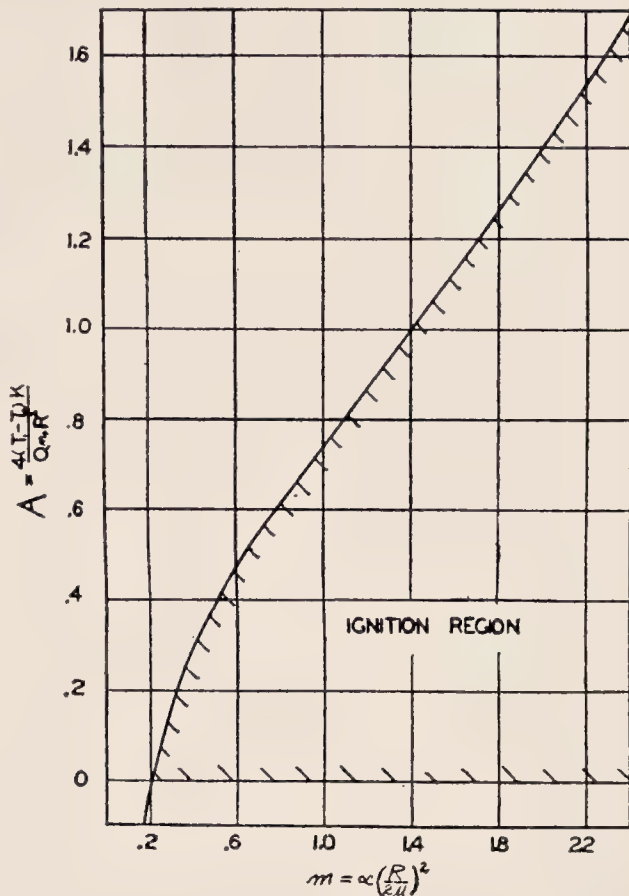


FIG. 2. Condition for ignition.

approaches $+\infty$ as x approaches 0 or ∞ for $m > 0$. By differentiation it is found that $F(x)$ has a single minimum given by the following relation between x and m .

$$m = x^2 \left[x^2 \left(\frac{\operatorname{erf} x + \frac{2}{\sqrt{\pi}} x \exp(-x^2)}{\operatorname{erf} x - \frac{2}{\sqrt{\pi}} x \exp(-x^2)} \right) - \frac{5}{2} \right] \quad (21)$$

From this there can be found the value of x which makes $F(x)$ a minimum for a given m , and then the value of $F(x)$ for this minimum. If A is not greater than this value, then from Eq. (20), $\partial T(0, t)/\partial t \geq 0$ for all t .

This then gives the desired relation which must be fulfilled for a nondecreasing temperature at the origin. It is that

$$A = \frac{4(T_1 - T_0)k}{Qn_0 R^2}$$

must be less than or equal to a value depending on α , since m is merely α expressed in convenient units. The ignition limit is, of course, given by the equality in this relation.

Figure 2 is a graph of the relation between A and α , and Fig. 1 shows the course of the temperature at the origin for five pairs of values of A and α .

Significance and Applicability of the Theory

Unfortunately the result obtained in the last section cannot be tested by direct comparison with experiment, because the quantities which enter have not been measured in experiments on the ignition of gases. In fact, they may be incapable of direct experimental determination. However, certain conclusions can be drawn from this theoretical result as it stands, and it should be possible to perform experiments which will give some information about the needed quantities.

From Fig. 2 it can be seen that ignition does not occur if $\alpha = 0$; that is, chain branching must take place for ignition to occur. This could have been expected to follow from the physical assumptions; because if the active particles do not increase in number, they eventually become very thinly spread out owing to diffusion and cannot generate enough heat to cause much rise in temperature. According to von Elbe and Lewis⁸ the chain-branching reaction in the oxidation of hydrogen is negligible at low temperatures. Our conclusion would then be that ignition of a hydrogen-oxygen mixture by a local source can only occur if the source raises some volume to a high enough temperature for branching to be significant. This statement sounds very similar to those made by the proponents of a thermal theory of ignition. However, it is obvious that our theory does not state that ignition is assured by merely raising some volume to a sufficiently high temperature. The statement above is simply a limitation in the case where branching is known not to occur at low temperatures.

There is one set of experimental data which, though not exactly fitting the conditions assumed here, can be shown to give at least qualitative agreement with the theory. Silver⁶ has studied ignition by shooting heated spheres of platinum and quartz into gases. He gives the minimum temperature to which spheres of various sizes must be heated to cause ignition in mixtures of 10 per cent coal gas, 3 per cent pentane, and 20 per cent hydrogen, each in air.

It is possible to relate Silver's experimental data to the considerations of this paper as follows: From Fig. 1 the condition for ignition is that

$$A = \frac{4(T_1 - T_0)k}{Qn_0R^2}$$

have a value which depends on

$$m = (R^2/4\mu^2)\alpha.$$

The relation between A and m is, over a considerable range, close to a straight line passing through the origin, so that

$$A = \text{constant} \times (R^2/4\mu^2)\alpha$$

is the ignition relation. Now α depends on temperature according to

$$\alpha = \text{constant} \times \exp -(E_1/RT)$$

also Q , being proportional to a reaction rate follows a similar relation,

$$Q = \text{constant} \times \exp -(E_2/RT).$$

The initial concentration of active particles probably depends on a surface reaction and can, therefore, also be assumed to be proportional to $\exp -(E_3/RT)$. Then

$$\frac{T - T_0}{R^4} = \text{constant} \times \exp - \frac{E_1 + E_2 + E_3}{RT}$$

and the graph of $\log [(T - T_0)/R^4]$ against T^{-1} should be a straight line. This graph is shown in Fig. 3 and it can be seen that the experimental values satisfactorily approximate a straight line.

The variation of k and c with temperature has been neglected. Inclusion of this factor would make no real difference in the appearance of Fig. 3; the slopes of the lines would be slightly increased.

Silver gave a theoretical discussion of his work, using as a criterion for ignition the requirement that the initial rate of heat production by the

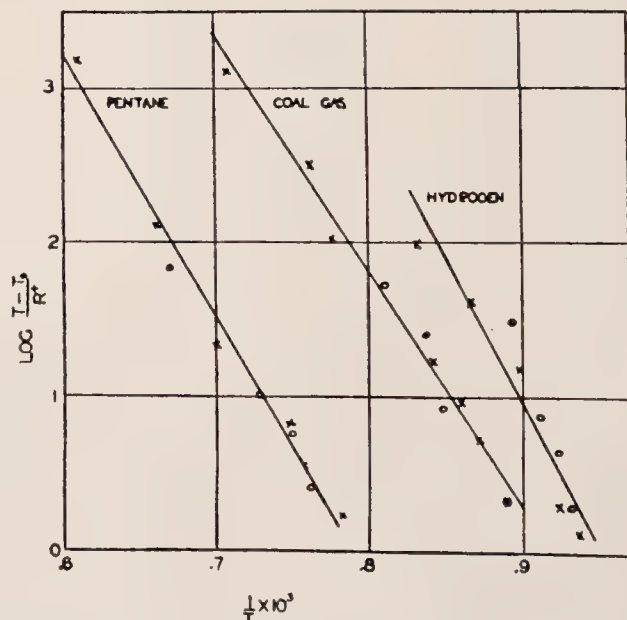


FIG. 3. Data of Silver (Ref. 6) on ignition of gases by heated spheres. Experimental values: \times , platinum spheres; \circ , quartz spheres.

reaction shall be greater than the rate of heat loss by conduction. This led to the conclusion that the graph of $\log [(T - T_0)/R]$ against T^{-1} should be a straight line with a slope equal to the activation energy of the reaction. The experimental points fell as close to straight lines as in the present analysis, but the slopes of the lines were approximately equal, whereas pentane and hydrogen have very different activation energies. The slopes of our lines are also not very different, but this is not contrary to the theory, since they should be proportional to $E_1 + E_2 + E_3$.

In the experiments just discussed, T_1 , the initial temperature of the sphere, was determined directly. This is one of the quantities needed to test the theory, but in the case of an electric discharge it appears to be impossible to relate T_1 to measured quantities. This suggests that it might be worth while to perform experiments with an energy source that released a known amount of energy, perhaps something like a percussion cap. It should then be possible to make statements about T_1 . This would be of value not only for testing the present theory, but should also put an end to the controversy over the thermal theory of ignition by giving a direct answer to the questions involved.

To test the present theory it is also necessary to have information about n_0 , the initial concentration of chain carriers. This requires a knowledge of the kinetics of the reaction and of the physical mechanism of the creation of these initial chain carriers.

If such information were available, it would be possible to make statements such as the following. Suppose T_1 is held constant, then for a given mixture α and Q should be constant. Let R and n_0 , vary then from

$$\frac{4(T_1 - T_0)k}{Qn_0R^2} = \text{constant} \times \frac{R^2}{4\mu^2} \alpha$$

Discussion

LOUIS S. KASSEL (Universal Oil Products Company, Chicago, Illinois): This paper certainly represents an interesting attempt to provide a mechanism for this important process. It may be worth while, however, to point out one feature of Landau's treatment that is perhaps oversimplified.

This is the assumption that the branching rate is independent of temperature; this admittedly incorrect proposition is justified by the statement that "the question as to whether ignition takes place or not is decided within a very short time." Inspection of Fig. 1, however, shows that when ignition fails the temperature at the origin may have risen, owing to the reaction, by 20 to 50 per cent as much

a relation of the form, $n_0R^4 = \text{constant}$, follows.

Again, if T_1 is constant and pressure, p , and R vary, a relation between p and R is obtained. The form of the relation depends on the kinetics of the reaction. Suppose that chain branching, α , requires the collision of m_1 molecules, that the heat-producing reaction involves m_2 molecules, and that the creation of the initial active particles involves m_3 molecules; then $\alpha = \text{constant} \times p^{m_1}$, $Q = \text{constant} \times p^{m_2}$, $n_0 = \text{constant} \times p^{m_3}$. Also μ^2 is inversely proportional to density, hence inversely proportional to pressure. So that the relation is $p^{m_2+m_3+1}R^4 = \text{constant}$.

If the theory could be verified for reactions for which the kinetics is fairly well established, it should be useful to test hypotheses about the mechanism of other reactions.

Acknowledgments

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as it had owing to the local source. Thus it is apparently required to assume that the branching rate is constant over a temperature interval of something like 100°C. It is to be expected that a theory which assumes a reasonable temperature coefficient for the branching rate will give a more rapid determination of whether ignition is to occur, and that failure to ignite will be preceded by only slight temperature rises. Even for these intervals, however, the increase of branching rate with temperature seems an essential feature of the theory, since it is only the effect of this increase which limits the abortive rise to a range over which one might think the branching rate could be considered constant.

IGNITION REGIONS OF HYDROCARBONS

D. T. A. TOWNEND

Imperial College of Science and Technology, South Kensington, London, England

Researches into the combustion of complex hydrocarbons, designed to throw light on the problem of knock in internal-combustion engines, have revealed generally that the mechanisms involved are far from simple. Much new light has recently been thrown on the subject by systematic investigation of the influence of pressure on the spontaneous ignition points of these materials.

Inflammable mixtures with air of the paraffins containing three or more carbon atoms, while not spontaneously ignitable at low pressures below about 500°C, give rise abruptly to ignition at higher pressures in a temperature range between about 310° and 370°C, where normally only "cool flames" are initiated; and although neither methane-air nor ethane-air mixtures appear to develop cool flames, the latter are ultimately ignitable in a lower temperature system less complex than that characteristic of the higher members. There is general agreement between ease of ignition in the lower temperature range and the knock ratings of the materials concerned. This holds good for side-chain paraffins, olefins, naphthenes, and aromatic fuels.

All olefins higher than ethylene behave in a similar manner; they differ from the paraffins in that the cool flames are less intense and the preflame time-lags are not only greater but decrease less rapidly with increase of pressure.

The influence of higher aldehydes, nitrogen dioxide, and diethyl ether as promoters of ignition is also discussed.

Introduction

Until comparatively recently any experimental evidence that the influences of such factors as varying temperature, pressure, or dilution on chemical reactions were other than in accord with simple laws would have been received by chemists with reserve, yet today many such apparent anomalies are recognized and their frequent occurrence in elementary combustion processes has contributed much evidence largely drawn upon in the development of the theory of chain reactions.

It is not surprising, therefore, that investigations into the combustion of complex hydrocarbons, designed in the first place to throw light on the problem of "knock" in internal-combustion engines, have shown when extended over wide enough temperature and pressure ranges that the mechanisms involved are far from simple; for such combustions are known to give rise to a variety of intermediate oxidation products, the concentrations of which at any stage of the reaction depend upon temperature, pressure, mixture composition, and environmental influences (cf. Newitt et al.¹⁷⁻²¹).

Systematic work on the influence of reaction temperature on the slow combustion of the higher paraffins, etc., in admixture with air was first published in 1929 by Pope, Dykstra, and Edgar^{27,2,8} who, working in a flow system, established that, although initial oxidation commenced at 150°-200°C, becoming active between 250° and 270°C in which range the products were

luminescent and then mildly explosive (cool flames) between 270° and 300°C, at higher temperatures the combustion was less rapid until about 500°C had been reached. Parallel observations were also made by Pease,²⁴⁻²⁶ and a temperature range in which a negative temperature coefficient of reaction velocity occurred became recognized. Edgar also produced strong evidence that with straight-chain paraffins the methyl group at the end of the chain was first attacked with the formation of the corresponding aldehyde and water, the aldehyde being subsequently oxidized to a lower aldehyde, etc.; with side-chain isomers the same process occurred until the side chain was reached, when a ketone was formed, and since ketones oxidize more slowly than aldehydes the reaction was slowed down, the luminescent combustion being less intense.

About the same time the cool-flame phenomena were examined by Emeleus,¹⁰ who showed the emission from several combustibles to exhibit spectra which differed from that of their normal flames but had a series of bands in common, recently identified as due to energized formaldehyde (cf. Ubbelohde³⁶ and Konratjew¹⁴). Prettre²⁸ also studied the character of the cool flames observed with many combustibles in a flow system. They were not observed with methane and ethane; rich mixtures of propane, pentane, hexane, heptane, and octane gave rise to them in a temperature range usually between 230° and 300°C above which normal inflammation did not occur until about 600°C had been reached. Aldehydes and ether readily exhibited cool flames,

but amylene and amyl alcohol were the simplest olefin and alcohol, respectively, to give rise to them.

In 1933 Townend and Mandlekar,³⁵ while studying the influence of pressure on the slow combustion of butane-air mixtures in a static system, observed that although at low pressures spontaneous ignition did not occur below 500°C, on the attainment of a critical pressure which varied somewhat with mixture composition it occurred abruptly in a temperature range below about 370°C, which was later recognized as that in which only cool flames are normally observable. The matter was therefore systematically investigated and extended to cover a wide range of combustibles.

The determination of ignition points over wide ranges of pressure and temperature, with which this paper is concerned, has been very fruitful in throwing light on the whole problem, for they provide information of the precise circumstances in which a maximum reaction velocity may be obtained under variable experimental conditions. It is now proposed briefly to review the field which has been covered so far and to indicate the general direction in which the results are leading, more detailed discussions of the possible chemical mechanisms involved being embodied in other papers contributed to this symposium.

Ignition Regions of the Paraffins

In Fig. 1 curves have been drawn showing the influence of pressure on the ignition points of corresponding rich mixtures with air of methane,

ethane, propane, butane, and hexane (curves 1, 2, 3, 4, and 5). The curve for the methane-air mixture fell rapidly from above 700° to about 500°C as the pressure was raised to 5 atm; thereafter it fell progressively to about 460°C with increase of pressure to 300 atm. Similar curves have been obtained with other mixture compositions, that exhibiting the lowest ignition points having a methane content between 30 to 40 per cent ($\text{CH}_4:\text{O}_2$ ratio = 2:1). The intermediate products normally found in slow combustion of methane are methyl alcohol and formaldehyde; the characteristics of the ignition point curves of both these materials are much the same as found with methane, but the order of ease of ignition is formaldehyde > methyl alcohol > methane, and small additions of formaldehyde strongly promote the combustion of the other two combustibles.^{12,5}

With the ethane-air mixture (No. 2) at pressures up to 15 atm the curve was as found with methane, ignition now occurring at somewhat lower temperatures. At this pressure (and at about 430°C) a sharp inflection occurred, the ignition points following an imposed lower system, settling down to temperatures about 325°–340°C at 25 to 30 atm. Another interesting feature of the experiments was very long preignition time-lags recorded, for, whereas with methane these had increased progressively from 3 to 40 sec with fall in ignition temperature to about 460°C, with ethane the increase was from 20 sec at 550°C to a few minutes at 435°C, the point of inflection; thereafter the lengthening was very marked and at 325°–340°C the lags had reached two hours or more.

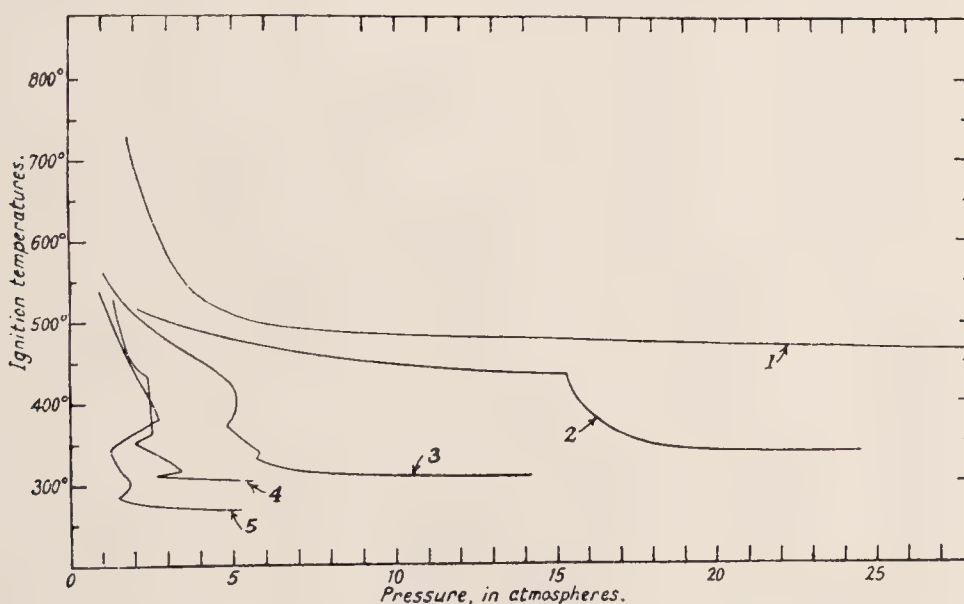


FIG. 1. Curves 1, 2, 3, 4, and 5 are for 13 per cent of methane, 10 per cent of ethane, 5 per cent of propane, 3.8 per cent of butane, and 2.7 per cent of hexane, respectively, in air.

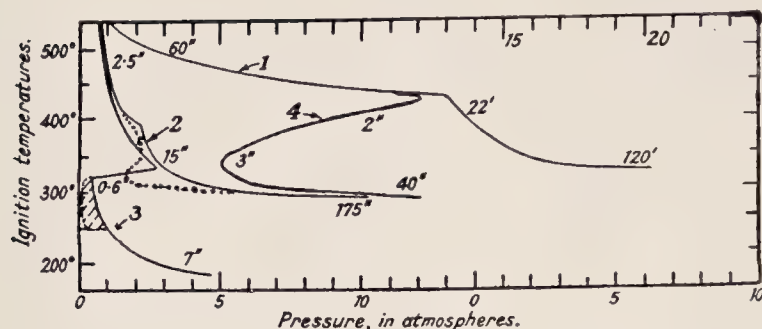


FIG. 2. Curves 1, 2, and 3 are for corresponding mixtures with air of ethane, ethyl alcohol, and acetaldehyde; curve 4 is as 1, but with addition of 1 per cent of acetaldehyde to the mixture.

With two carbon atoms in the molecule the number of intermediate compounds known in the intermediate products is greater than with methane, and it was thought not unlikely that at lower temperatures the longer life of some comparatively unstable material might well be responsible for the superposed lower ignition system; in particular acetaldehyde, which is known strongly to promote the combustion of ethane at 316°C ,⁷ might well function in this way. This was soon borne out by a comparative study of the ignition point curves of ethane (with and without addition of acetaldehyde), ethyl alcohol, and acetaldehyde (Fig. 2, curves 1, 4, 2, and 3).

A comparison of curves 1 and 4 leaves little doubt that the superposed lower system found with ethane was in some way attributable to the formation of acetaldehyde during slow combustion, for the addition of 1 per cent of it to the mixture not only markedly promoted ignition in the lower system but reduced the time-lags from more than two hours to a few seconds. Moreover, this effect was limited entirely to the lower system, for above 435°C the aldehyde had no influence whatever; if anything, it tended to retard the ignitions. This result also throws an interesting light on the apparent disagreement between the observation of Bone and Hill,⁷ who found that the presence of 1 per cent of acetaldehyde caused the ignition of an ethane-oxygen mixture at 316°C and 710 mm pressure under conditions when normally the reaction proceeded quite slowly, and the more recent observation of Steacie and Plewes,³² who found that with a $\text{C}_2\text{H}_6 + 2.3 \text{ O}_2$ mixture at 452°C , acetaldehyde, while virtually eliminating the "inhibition" period, had little or no effect upon the subsequent oxidation of the ethane.

The curve for the ethyl alcohol-air mixture (No. 2) also exhibited a superposed lower system ignition occurring at much lower pressures over the whole temperature range than with the corresponding ethane-air mixture (No. 1); moreover the presence of 1 per cent of acetaldehyde in the mixture (dotted curve) exhibited a like effect to that found with the ethane-air mixture. Finally, determinations of the ignition points of

acetaldehyde-air mixture (No. 3) left little doubt that the formation of acetaldehyde was responsible for the characteristic curves of ethane and ethyl alcohol, for at temperatures above about 330°C a strong negative temperature coefficient of reaction velocity was apparent, a "throw back" in the ignition point curve being observed. It should also be mentioned that cool flames were observed for the first time with acetaldehyde-air media, and that they occurred within the temperature and pressure limits defined approximately by the dotted boundary curve enclosing the shaded area. When true ignition occurred in this temperature range at an adequately high pressure (defined by curve 3), it always followed at a definite short time interval following the formation of a cool flame. The simplest interpretation of these results would seem that at the upper temperature limit of the lower system the life of intermediately formed acetaldehyde is inadequate to promote the combustion as a whole; it may equally well be, however, that this applies to some product to which the aldehyde gives rise or, alternatively, that some other process sets in which renders the aldehyde innocuous; pending further chemical evidence, however, judgment should be suspended.

Reverting again to Fig. 1, curves 3, 4, and 5, pertaining to propane-, pentane-, and hexane-air mixtures, it will be observed that with all paraffins containing three or more carbon atoms an abrupt fall in the ignition points occurred, an important observation being the occurrence of two pressure minima of ignition, one at about $280^{\circ}\text{--}330^{\circ}\text{C}$ and the other at about $340^{\circ}\text{--}370^{\circ}\text{C}$, both being lowered progressively as the hydrocarbon series was ascended. These observations have recently been extended by Mr. M. McCormac in these laboratories to cover heptane, octane, and decane, with results which are in conformity with the behavior of the lower members of the series.

It is also important to note that as the series was ascended not only did the minimum pressures for ignition in the lower range decrease, but the preignition time-lags were also materially reduced; for instance, with propane lags of the

order of 3 to 5 sec were reduced to less than 1 sec with hexane.

With members containing three or more carbon atoms there were also fairly well defined pressure and temperature limits within which cool flames were propagated, those for three propane-air mixtures containing 2.6, 5.0, and 7.5 per cent of the combustible being illustrated by the diagonally shaded areas associated with the ignition point curves, Nos. 1, 2, and 3 in Fig. 3. When cool flames were propagated a slow-moving, pale bluish flame was observable through the windows provided in the explosion vessel; this was accompanied by the development of a small pressure pulse and a considerable formation of intermediate compounds strongly aldehydic in character. The phenomenon was quite different from normal flames which are usually fast travelling, giving rise to a whitish emission and high pressure development, the products containing only traces of intermediate compounds. As will be shown later the cool flames occurred after a definite time-lag which was usually of the order of 20 to 30 sec at the lower temperature boundary; as at any selected pressure the temperature was raised, these lags were appreciably shortened and the cool flames became more intense up to about 360°C. Above this temperature the lags became very short and the intensity of the flames rapidly diminished, until above the upper temperature limit they were no longer observable. At a stated temperature the cool

flames also increased in intensity as the pressure was raised from the lower pressure limit; and when a pressure adequate for true ignition was attained a two-stage process occurred, the full ignition following rapidly after the formation of a cool flame. Such behavior may be regarded as characteristic of all the higher paraffins.

It should perhaps be stated here that the method employed in the determinations so reviewed was that which originated with Mallard and Le Chatelier, the mixture under investigation being admitted rapidly into an evacuated vessel maintained at the experimental temperature; the vessel employed had a cylindrical cavity 17 cm \times 3.75 cm, capacity = 170 cc, and was provided with a mild-steel liner. If liners of other materials were employed, ease of ignition seemed to depend on their catalytic inactivity; moreover, alteration in the dimensions of the cavity, while influencing the precise location of the curves according to circumstances, was without effect on the general character of the phenomena. Due to the extreme violence of the ignitions usually found when undiluted combustible-oxygen mixtures were employed (particularly with those containing excess of oxygen) and also because a main interest has been in correlating ease of spontaneous ignition under pressure with the known "knocking" propensities in engine practice of the fuels concerned, the investigations so far completed have been mainly restricted to mixtures made with air. Recently, however, Newitt

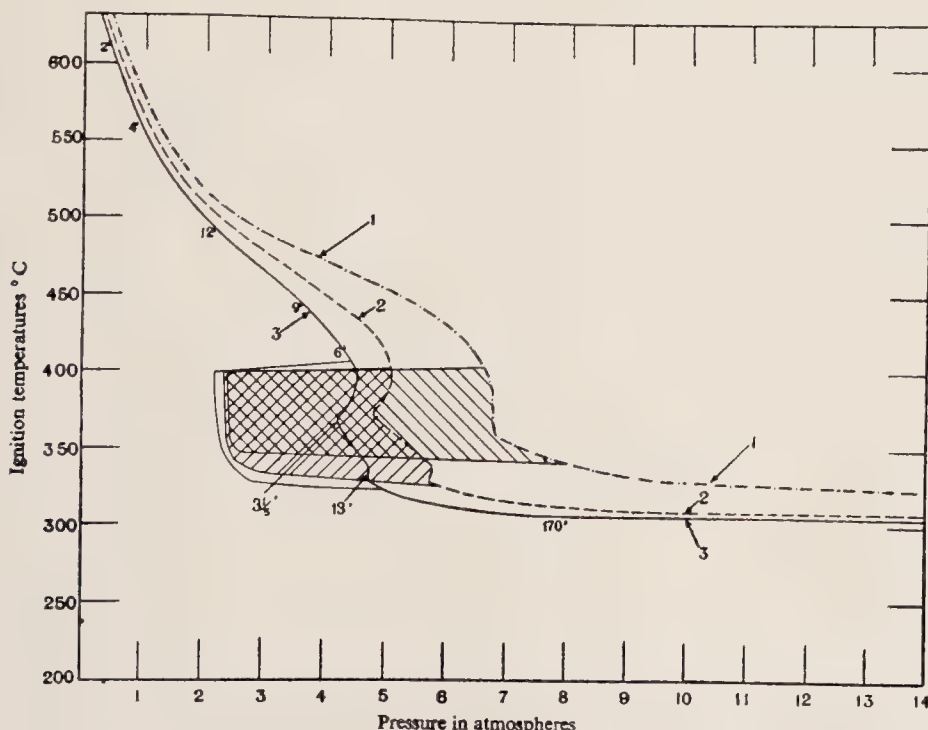


FIG. 3. Propane-air mixtures. Percentage mixtures for the curves: curve 1 = 2.6; curve 2 = 5.0; curve 3 = 7.5

and Thornes²² have made a close examination both of the ignition characteristics of an equimolecular propane-oxygen mixture in silica vessels and also of the intermediate products at all stages of the combustion, which has thrown further light on the subject; of particular interest has been their observation that in certain circumstances it is possible for as many as five cool flames to succeed one another. Elsewhere, Neumann and his collaborators¹ and Prettre²⁹ have studied the behavior in the cool-flame regions of mixtures of butane and pentane with oxygen, their observations agreeing in all essentials with those already described but being more directed towards their kinetic interpretation.

The Relationship between Spontaneous Ignition and Knock

It is now generally recognized that the behavior of any fuel in an engine is largely influenced by the chemical reactivity of the unburnt medium ahead of the flame (cf. Refs. 9, 37, 38, and 30), this being controlled by the degree of compression, the working temperature, and speed of running. In such circumstances where the available time interval is short any appreciable chemical reaction must *ipso facto* be intense, and conditions will proximate closely to those of the ignition point; indeed, since the work of Tizard and Pye³³ it has been well appreciated that there is in general a close relationship between both

ignition points and temperature coefficients of reaction velocity of fuel-air media and their knocking propensities in an engine. There have been, however, certain practical difficulties to an unqualified acceptance of this relationship; also, although it was early recognized that a limit was set to engine design by critical compression ratios depending on the fuel employed, the part played by pressure other than by raising the working temperature remained obscure, there being no reason to suppose that its influence on ignition points was abnormally great and other than quite progressive.

When it was discovered with the higher paraffins that (1) the lower ignition region approximated to the ordinary compression temperatures attained in an engine, (2) ignition occurred abruptly in this region with a minimum time-lag on the attainment of a critical pressure, while at higher temperatures the mixtures were non-ignitable, (3) mixtures rich in combustible ignited at a lower critical pressure than those containing excess of air, (4) not only did ignition occur at progressively lower pressures as the series was ascended but the time-lags were also materially reduced, and (5) the presence of an antiknock raised the pressure necessary for ignition, it became clear that it was to the pressure requisite for ignition in the lower range that the standard knock ratings of fuels were probably related.

In considering the ignition point determina-

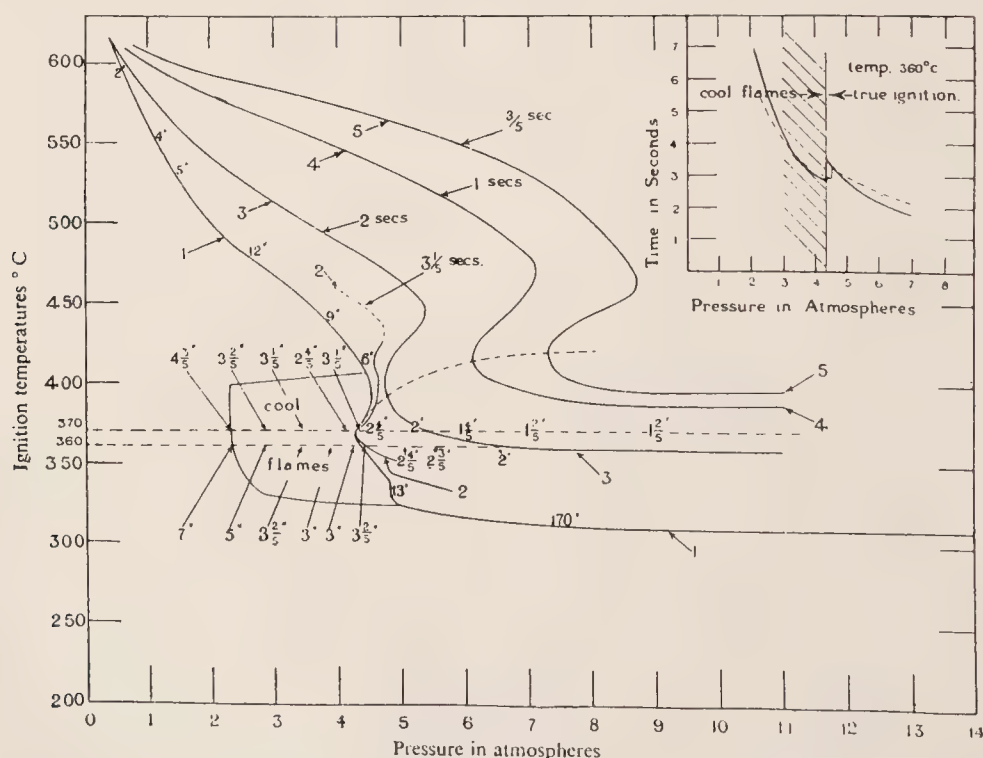


FIG. 4. Influence of pressure on time-lags. 7.5 per cent propane-air mixture

tions in the light of their probable application to internal-combustion engines, however, the question of time-lag was of predominating importance, because in such conditions the maximum lag permissible would not exceed a few thousandths of a second. It is not possible with the method of working in the investigations described here to determine with precision lags of much less than 0.5 sec. Propane-air mixtures, however, while exhibiting the behavior characteristic of the higher paraffins generally, have much longer time-lags than found with the higher members, so that it was possible to indicate the general influence of pressure on them.

In Fig. 4, curve 1 shows the ignition points of a 7.5 per cent propane-air mixture plotted against pressure in the ordinary way; the lags printed against the curve were those at these minimum ignition pressures and as previously pointed out they were variable, being usually shortest in the cool-flame temperature range. The figures in the cool-flame area are the lags observed at 360° and 370°C prior to the appearance of a cool flame; they decreased with increase of pressure and corresponded with the lags observed for true ignition when the requisite pressure had been attained. [Cf. inset, Fig. 4. When true ignition occurred the lags showed a slight increase due to the two-stage process already referred to. The dotted curve shows the lags for the same mixture, but with an addition of 0.05 per cent of lead tetraethyl.] The temperature of minimum lag on curve 1 was found at about 370°C; at higher and lower temperatures on the curve this lag increased, but by increasing the pressure above the minimum the lags were shortened. Curve 2 is the curve so plotted for ignition with a lag of 3.2 sec. Similarly, curves 3, 4, and 5 were plotted for lags of 2, 1, and 0.6 sec, respectively.

Marked pressure minima persist in the iso-lag curves at higher pressures, an interesting feature being that the temperatures at which the minima are located do not remain fixed but show an immediate sharp rise from 370° to 415°C, thereafter apparently remaining constant; this temperature corresponds with the upper limit for cool flames. Also when the time-lags become short by increasing initial pressure the ignitions are extremely violent and akin to detonation, a matter which is being further investigated by Dr. G. P. Kane in these laboratories.

With higher hydrocarbons (cf. hexane³⁴) an iso-lag curve of the type shown by No. 5, Fig. 4, would relate to extremely short lags, immeasurable without special methods; and when it is recalled that the compression temperature of the working fluid in an engine varies with the compression ratio employed somewhat as follows: 4:1, 385°C; 5:1, 410°C; 6:1, 430°C (although in

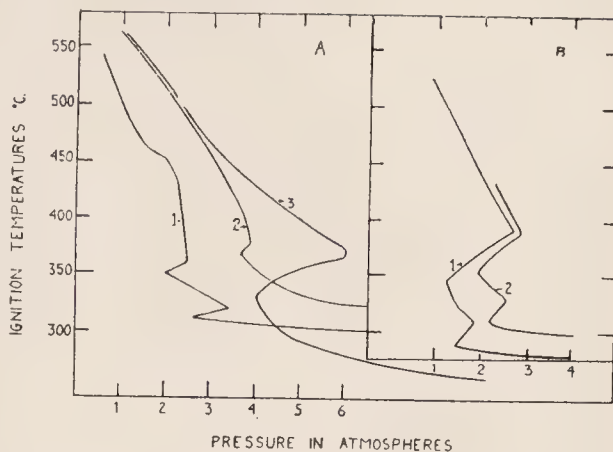


FIG. 5. (A) Theoretical mixtures with air of butane (curve 1), isobutane (curve 2) and isooctane (curve 3). (B) Theoretical mixtures with air of hexane (curve 1) and cyclohexane (curve 2).

engine practice other factors such as dilution with explosion products, the formation of reaction centers during the compression stroke, and the part played by the advancing flame call for consideration), there would seem little doubt at all as to the general significance of the curves. Incidentally also it is clear why slow running is conducive to knock for, although this has been attributed in some quarters to better volumetric efficiency, it is more likely due to the increased available lag period.

While so far we have confined this discussion to the straight-chain paraffins, it remains to state that no exception has yet been found to the relationship between knocking propensity of any fuel and the pressure requisite at the compression temperature for its spontaneous ignition within a short time-lag. Thus the knock ratings of ethane, ethyl alcohol, and acetaldehyde (14.0, 7.5, badly knocking) would be inferred at a glance from the curves in figure 2. To illustrate the behavior of side-chain paraffins, in Fig. 5(A) the ignition point curves of corresponding mixtures with air

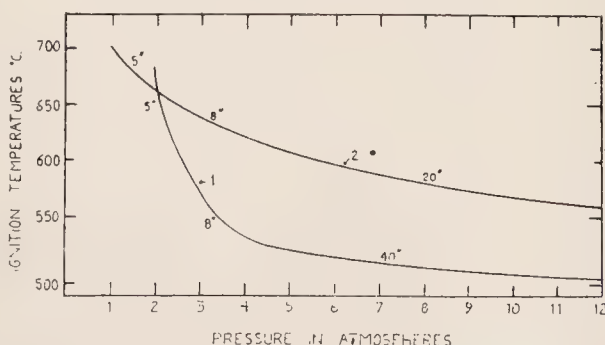


FIG. 6. Theoretical mixtures with air of methane (curve 1) and benzene (curve 2). Small figures along the curves denote time-lags.

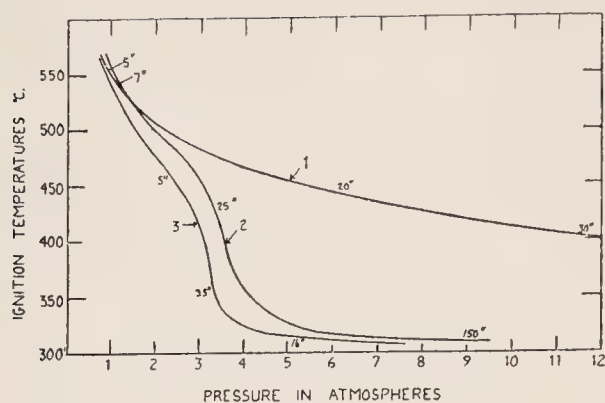


FIG. 7. Theoretical mixtures with air of ethylene (curve 1), propylene (curve 2), and butylene (curve 3). Small figures along the curves denote time-lags.

of butane, isobutane, and iso-octane (2,2,4-trimethylpentane) have been drawn (curves 1, 2, and 3). Figure 5(B) contrasts the behavior of mixtures of hexane and cyclohexane (curves 1 and 2). Materials such as methane and benzene,¹¹ which do not knock, exhibit ignition point curves which apparently show no lower system at all (curves 1 and 2 in Fig. 6). The behavior of the simpler olefins will now be described.

Ignition Regions of the Simpler Olefins

Recently Kane and Townend¹³ published an account of an extension of the investigations into the influence of pressure on the spontaneous ignition of hydrocarbon-air media to the simpler α -olefins: ethylene, propylene, butylene, and amylene. In Fig. 7, curves 1, 2, and 3 show the influence of pressure on the ignition points of theoretical mixtures with air of ethylene, propylene, and butylene.

With the ethylene mixture (No. 1) the ignition points fell progressively with increase of pressure, a smooth curve of the type previously observed with methane-air mixtures being obtained. There was never any indication of the formation of cool flames, even though the curves for rich mixtures fell to about 300°C at sufficiently high pressures, nor was any irregularity in the time-lags observed; these increased from 4 to 5 sec at 550°C to about 30 sec at 370°C and 240 sec at 310°C, varying slightly with mixture composition.

The fact that the ignition point curves for ethylene-air mixtures are quite smooth and that no superposed lower system as found with ethane-air mixtures was observed is a matter of interest, because, as has already been pointed out, strong evidence was adduced that with ethane this was attributable to an adequate formation of

acetaldehyde, which is a principal product in its slow oxidation. If this be correct it seems possible that the known formation of acetaldehyde in the slow combustion of ethylene^{6,15,17} arises not as a direct immediate oxidation product but as the outcome of a slower secondary process less likely to influence ignition. This would be in agreement with the view that acetaldehyde arises by an isomeric change from a primary product (cf. Bone⁴ and also with Norrish's atom chain mechanism as applied to ethylene.²³ Formaldehyde, on the other hand, which is known to promote the main combustion⁶ was always a product of the preflame combustion and the curve is consistent with its playing such a role, as in fact it does with methane (cf. p. 135).

Pressure had a far more marked influence on the ignition points of the propylene-air mixture (No. 2). The ignition points fell progressively at the lower pressures to about 440°C; further increase of pressure, however, caused an abrupt fall over a temperature range where cool flames were also observable, but below about 330°C increase of pressure had little further influence. Although the ignition points fell rapidly no irregularities in the time-lags were observed; in this respect and in the fact that the curves showed no pressure minima propylene differs from propane. A study of the respective behaviors of propane and propylene may better be made by comparing Fig. 8, which shows both the ignition point curves and the cool-flame areas for three propylene-air mixtures containing 3.0, 4.5, and 6.0 per cent of the combustible, with Fig. 3. The main difference, however, lay in the weakness both of the pressure pulses and of the luminosity associated with the cool flames of propylene, a

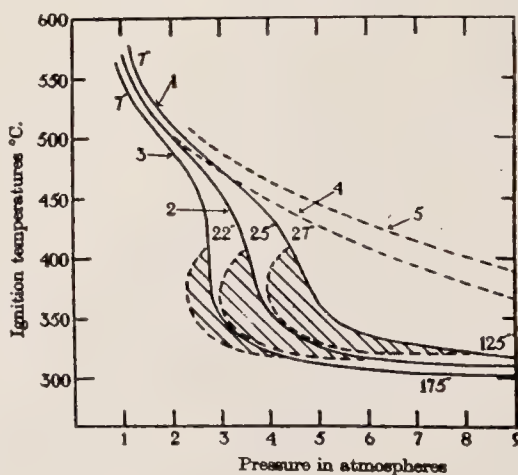


FIG. 8. Propylene-air mixtures. Percentage mixtures for the curves: curve 1 = 3.0; curve 2 = 4.5; curve 3 = 6. Curves 4 and 5, for the 4.5 per cent mixture, relate to ignition with constant lags of 3 and 2 sec. Shaded areas indicate cool-flame regions.

fact which made impossible precise determinations of the pressure and temperature limits for them. Moreover, although for corresponding mixtures those with propylene were ignitable at slightly lower pressures than those of propane, not only were the time-lags longer with the former but their rate of decrease with increase of pressure was not as great; curves 4 and 5, in Fig. 8, relate to ignitions of the 4.5 per cent mixture No. 2 with a constant lag of 3 and 2 sec, respectively, and may be compared with the curves for a 7.5 per cent propane-air mixture (Fig. 4).

The ignition point curve for the α -butylene-air mixture (No. 3, Fig. 7) resembled closely that obtained with the propylene-air mixture, the minimum ignition points, however, occurring at lower pressures. Although there was still no indication of pressure minima of ignition in the lower temperature range characteristic of the higher paraffins, the lags, which were much shorter than those observed with either ethylene or propylene, showed an irregularity in this range as found with the paraffins; thus they were reduced from about 5 sec at 450°C to a minimum value of 3.5 sec at 370°C, thereafter increasing to 16 sec at still lower temperatures. The cool flames were also more pronounced in regard to both the accompanying pressure pulses and luminosity.

Amylene as supplied commercially (b.p. 36°–40°C) consists of side-chain isomers. A small quantity of α -amylene (b.p. 30.3°C) was specially synthesized, but only sufficient was available to complete the ignition point curve of a mixture containing 2 per cent of it (theoretical mixture,—2.7 per cent); this is shown in Fig. 9, No. 1. Other curves were determined with a sample of purchased material containing more stable isomers;

No. 2 relates to a 2 per cent mixture of this material.

The ignition points of the α -amylene mixture (No. 1) gave for the first time definite evidence of the pressure minima in the cool-flame temperature range, invariably found with the higher paraffins; the higher minima occurred at 340°C and the lower at 312°C. The time-lags were also irregular as with the paraffins, a minimum value of 1.8 sec being observed at 340°–350°C. Cool flames were observable between 310° and 410°C, the pressure pulses being marked between 310° and 360°C. Moreover, as would be anticipated, the mixture of the side-chain isomers No. 2 was not nearly as easily ignitable as that of the α -olefin.

Comparison of the Respective Behavior of Paraffins and Olefins

From the results obtained with the four simpler olefins it may be stated that the influence of pressure on their spontaneous ignition in admixture with air is not unlike that found with the paraffins. Thus, ethylene behaves like methane, and although propylene and butylene did not reveal strong negative temperature coefficients of reaction as found with the corresponding paraffins, the ignition point curves exhibited a sharp fall over narrow critical pressure ranges to a lower system where cool flames were normally observed; and finally a 2 per cent α -amylene-air mixture showed all the characteristics typical of higher paraffin-air mixtures.

Also the minimum pressures requisite for ignition in the lower temperature range with corresponding mixtures, considered in the light of the observed time-lags, indicate that the knock ratings of both olefins and paraffins should fall as the series is ascended. This is in accord with the "critical compression ratios" of Boyd, as Table I shows. The results of the investigation as a whole are, in fact, in conformity with the general conclusions of Boyd,¹⁶ that (1) in an homologous series, whether paraffinic or olefinic, the tendency to knock increases with increasing length of the saturated carbon chain, and (2) in an isomeric series, knock decreases progressively with the centralization of the double bond.

Reverting to the chemical processes operative in the combustion of either paraffins or olefins containing more than three carbon atoms, at least three conditions call for consideration: namely, (i) that giving rise to cool flames in the temperature range usually between about 280°–410°C; (ii) that ultimately resulting in true ignition in the products from cool flames, there being usually two distinct zones of activity, (a) 300°–330°C and (b) 340°–370°C, respectively;

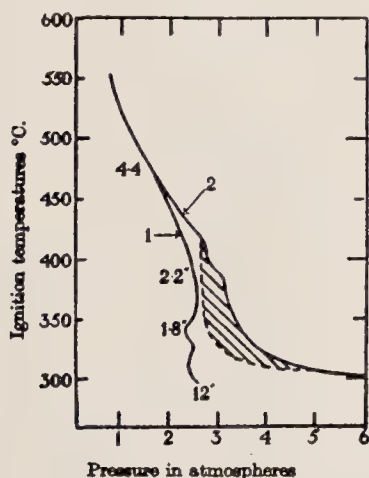


FIG. 9. Amylene-air mixtures. Curve 1 = 2 per cent of α -amylene; curve 2 = 2 per cent of isomeric amylene.

TABLE I

Comparison between critical compression ratios and minimum ignition pressures

Hydrocarbon	Critical compression ratio (Boyd)	Minimum ignition pressure at 350°C, atm	Time-lag, sec
Olefins:			
Ethylene	8.5		
Propylene	8.4	5.0	30
α -Butylene		3.35	3.5
α -Amylene	5.8	2.4	1.8
Paraffins:			
Ethane	14		
Propane	12	6.8	3
Butane	6.4	3.4	2
Pentane	3.8	2.2	1.4
Hexane	3.3	1.9	1
Isobutane	8.9	4.4	3

and (iii) that occurring above the upper limit for cool flames, i.e., above about 410°C. It would seem that with most fuels, conditions conducive to (i) are mainly responsible for knock,* and that the phenomenon itself involves essentially the processes occurring in (ii) which are intense at sufficiently high pressures.

There is little doubt that the processes giving rise to cool flames are of a chain character and probably associated with the presence of higher aldehydes and other active intermediate bodies. That aldehydes are important intermediate products may be seen from Fig. 10, which shows the ignition points of a 7.5 per cent propane-air mixture, No. 1, which contains defect of air with which 1 and 2 per cent of propionaldehyde, Nos. 2 and 3, and 1 and 2 per cent of acetaldehyde, Nos. 4 and 5, had been admixed. The influence of acetaldehyde on the cool-flame area has also been illustrated. There is little difference in the behavior of the two aldehydes in facilitating ignition; both induce ignition in the lower temperature

* This holds without doubt for fuels of "critical compression ratios" < 6 to 8. At higher compression ratios the compression temperature would doubtless approach 500°C, which is probably in the upper ignition range even with very short time-lags. It is significant that propylene (C.C.R. = 8.4) is the only olefin to exhibit a knock rating lower than that of the corresponding paraffin (C.C.R. = 12), and reference to figures 4 and 8 shows that whereas in the lower range the iso-lag curves for propane occur at much lower pressures than with propylene, in the higher range the reverse is true.

range at much lower pressures and temperatures than are observed with the simple mixture, and both have much less influence on the ignition points at higher temperatures and comparatively none above 550°C. A similar effect was also found on addition of 1 per cent of acetaldehyde to a 4.5 per cent propylene-air mixture.

While the behavior of the α -olefins under pressure is not unlike that of corresponding paraffins, the main difference lies in the reduced luminosity of the cool flames and the feeble pressure pulses observed with them, indicating that the processes operative in the low-temperature system are less intense than with the paraffins; moreover the preflame time-lags were not only greater but decreased less rapidly with pressure. There would seem no reason to postulate any difference in the intermediate products (or chain initiators) responsible for promoting reaction with both homologs, and these probably result from the formation of higher aldehydes. This view would be in agreement with the well-known researches of Beatty and Edgar.² Kane and Townend¹³ regarded the degenerate branching view of Semenov³¹ as attractive in explaining their results, for the less vigorous behavior of the olefins may be attributable either to a slower building up of active centers depending upon aldehyde concentration by virtue of difference in the chemical stages involved, or to the intervention of stronger in-

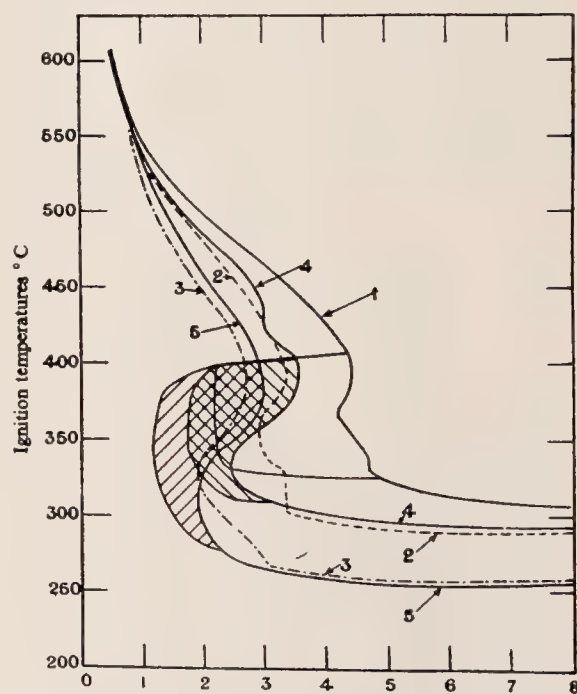


FIG. 10. Curve 1 = 7.5 per cent propane-air mixture; curves 2 and 3 = the same with addition of 1 and 2 per cent of propionaldehyde; curves 4 and 5 = the same with addition of 1 and 2 per cent of acetaldehyde.

hibiting processes. The former explanation is readily interpretable by comparing the respective stages involved in building up higher aldehydes from propane and propylene (cf. Refs. 3, 23). With regard to the kinetics of the chain mechanisms involved, Aivazov and Neumann¹ have developed an empirical equation agreeing closely with experiment for the relation between the preignition time-lags for cool flames, which are regarded as ignitions giving rise to stable intermediate products, and the experimental temperature, pressure, vessel diameter, and minimum cool-flame pressure. Their expression is based on Semenov's theory of spontaneous ignition as arising by a process of interacting chains in accordance with the expression

$$dn/dt = n_0 r - (g - f)n + f^1 n^2,$$

where n_0 = the number of active centers formed, r = the length of the primary chain, g = the chain-breaking factor, f = the chain-branching factor, and $f^1 n^2$ takes account of chain interaction, f^1 being small. No suggestions are made, however, as to either the character of the interacting centers or the products likely to be produced from them. Prettre²⁹ has also related the time-lags observed with pentane-oxygen mixtures with a simple chain mechanism.

No complete explanation has so far been forthcoming to account for the upper temperature limit for cool flames. Recent experiments on ether-air mixtures in these laboratories leave little doubt that the mechanisms operative are the same whether the flames are ignited artificially in cold media by means of a hot wire or whether they are developed spontaneously in a sufficiently heated vessel. It would appear that for some reason there is an upper temperature barrier to the flames which is never exceeded. This may possibly be due to thermal instability or elimination by other means of a chain initiator or material giving rise to a chain initiator; or it may also well be that an intermediate product (e.g., acetaldehyde) breaks down by a chain process. From a thermal point of view the temperature restriction may perhaps be likened to the limitation imposed in high-temperature flames by the dissociation of carbon dioxide and water; an important clue would seem to be the presence in the flames of energized formaldehyde.

The Influence of Nitrogen Dioxide

Interesting light on the problem has recently been thrown by studying the influence of small amounts of nitrogen dioxide on the ignition points.¹³ In Fig. 11(A) the influence of successive additions of 0.1 and 1 per cent of nitrogen dioxide to a 7.5 per cent propane-air mixture (curve No.

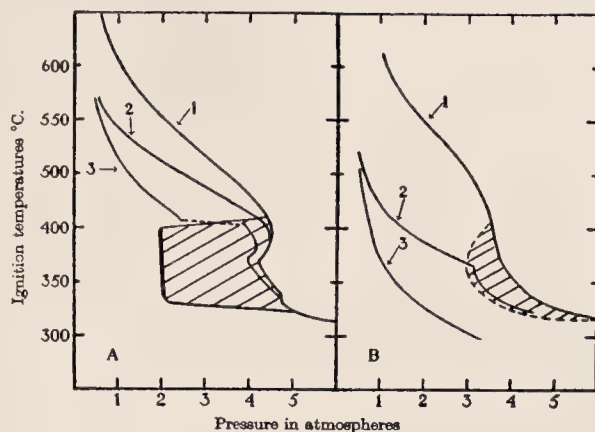


FIG. 11. (A) Curve 1 = 7.5 per cent propane-air mixture; curves 2 and 3 are the same but with 0.1 and 1.0 per cent additions of nitrogen dioxide. (B) Curve 1 = 4.5 per cent propylene-air mixture; curves 2 and 3 are the same but with 0.1 and 1.0 per cent additions of nitrogen dioxide.

1) may be seen from the corresponding ignition point curves (Nos. 2 and 3). By far the greatest influence of the promoter was not only to reduce the time-lags, but to effect ignition at much lower pressures in the temperature range above the upper limit for cool flames. There now appeared, in fact, an abrupt transition from the sensitized ignition typical of the upper system to ignition arising as a sequence of cool-flame formation, as indicated by the dotted line (curve No. 3). Thus in the low-temperature range the presence of nitrogen dioxide had by comparison no great influence in extending the cool-flame limits, and the ignition limits while being slightly reduced at temperatures between about 330° and 400°C were, if anything, raised at lower temperatures.

There was thus important and independent evidence of different chemical mechanisms in the two ignition ranges, and the results suggest the possibility of mutual destruction of active centers in the lower system. The comparative ineffectiveness of nitrogen dioxide in promoting combustion in the cool-flame range is of great interest, because it is in keeping with the observation of Egerton and collaborators^{9,37} that it was without influence in inducing knock with butane, heptane, and petrol, although with hydrogen it did so.

In Fig. 11(B) a corresponding set of curves has been drawn showing the respective influence of addition of 0.1 and 1 per cent of nitrogen dioxide (curves 2 and 3) to a 4.5 per cent propylene-air mixture (curve 1). Apart from reduction in the time-lags the presence of nitrogen dioxide was still without influence on the limits within which cool flames were observed. With regard to true ignition, however, the presence of 0.1 per cent of nitrogen dioxide not only very greatly reduced

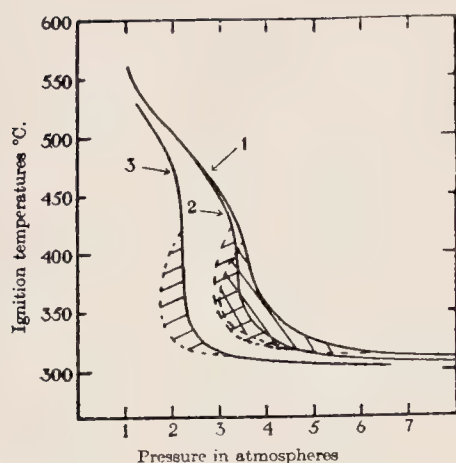


FIG. 12. Curve 1 = 4.5 per cent propylene-air mixture; curves 2 and 3 are the same but with 0.1 and 0.5 per cent additions of diethyl ether. Shaded areas indicate cool-flame regions.

the limiting pressures in the upper system but promoted ignition resulting in the lower system in the cool-flame products (curve 2); and 1 per cent of it so sensitized the combustion that a smooth curve (No. 3) was obtained, ignition occurring over the whole range without any apparent prior cool-flame reaction whatever. This marked difference in the relative influence of nitrogen dioxide in the lower system with propane and with propylene seems in agreement with the views already expressed concerning the two combustions, for the rate of chain development with propylene, which is by comparison with propane a slow process, would be the more enhanced by the addition of active centers to the system.

The Influence of Ether

It is well known that ether vapor when added to a fuel-air mixture acts as a strong proknock. Newitt's recent discovery²⁰ of the formation of mixed ethers in the slow combustion of olefins has revealed another class of intermediate compounds, the influence of which calls for investigation. In Fig. 12, curves 2 and 3 show the influence of additions of 0.1 and 0.5 per cent of ether to a 4.5 per cent propylene-air mixture (No. 1). Ether plays a role rather like, but much more powerful than, that of acetaldehyde, for 0.1 per cent of it (No. 2), while facilitating combustion in the lower range below 425°C, was without influence at higher temperatures; an addition of 0.5 per cent of it (No. 3), however, powerfully promoted the combustion, this being marked even up to 500°C. So far as the matter has been tested a similar effect has been found with propane-air mixtures.

The interpretation of the respective influences of higher aldehydes, ether, and nitrogen dioxide on the combustion as described is now forming the subject of further investigation.

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THE SLOW COMBUSTION OF GASEOUS PARAFFINS, ESPECIALLY PROPANE

ROBERT N. PEASE

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

In the slow oxidation of propane at 270°–280°C it has been found that treating the Pyrex reaction bulb with potassium chloride greatly lengthens the induction period, thus indicating that the preliminary reaction occurs on the surface. Addition of small amounts of acetaldehyde shortens but does not eliminate the induction period, a fact which confirms previous conclusions that peracids (formed from aldehyde) are unimportant in the reaction scheme. Experiments after the potassium chloride treatment show that conditions favoring access to the walls diminish the rate of reaction markedly. This, together with the previously observed destructive action of the treated wall on peroxides, indicates that the latter play an essential role in the slow oxidation of the higher paraffins, whatever may be the case for methane and ethane.

The nonexplosive oxidation of gaseous paraffins, which occurs at about 300°C and 1 atm, has as its outstanding characteristic a lengthy induction period. During the minutes or hours that this may take to complete itself, some infinitesimal alteration of the reaction system must be taking place. In his original work on ethane, Bone² limited himself to the suggestion that "the gases (or at least one of them) were merely 'getting ready' in some way." Later work on methane revealed that the reactants were not entirely inert during the induction period. Toward the end, small amounts of formaldehyde could be detected.¹ This fact, coupled with the observation that the formaldehyde increases to a maximum at the maximum reaction rate and that added formaldehyde can eliminate the induction period, points inescapably to this substance as the active intermediate.

If one were to conclude that the function of the formaldehyde is to introduce active oxygen into the system either as atoms³ or as peroxide oxygen,⁹ one might predict that higher aldehydes (e.g., acetaldehyde) would be even more efficient. This is, in fact, apparently just what has been observed in the case of ethane oxidation. Bone and Hill, found, for example, that with 1 per cent of acetaldehyde at 316°C explosion occurred. To be sure, this conclusion about active oxygen supplied by the aldehyde runs counter to the observation that potassium chloride largely eliminates peroxide oxygen without radically altering the rate of hydrocarbon oxidation.⁸ Nevertheless, the case is certainly a strong one, as von Elbe and Lewis have shown.

In view of the above, it was most surprising to find that acetaldehyde is by no means so efficient in inducing the oxidation of propane as it appears to be in the case of ethane. The experiments to be described in the following were undertaken to investigate the relation of the rate of oxidation

of propane to the propane and oxygen concentrations. In order to obtain measurably low rates it was necessary to reduce the temperature somewhat below 300°C, but when this was done the induction period became excessively long. To get around this difficulty small amounts of acetaldehyde vapor were introduced into the reaction bulb before the propane-oxygen mixture. The reaction was followed by pressure measurement.

It was found that with 300 mm. each of propane and oxygen at 280°C in the uncoated reaction bulb, the induction period ($\Delta P < 1$ mm) was 39 min and reaction was virtually completed in 5 min more. When 20 mm of acetaldehyde was first introduced into the reaction bulb a mild explosion occurred. With 2 mm of acetaldehyde, there was a 6-min induction period, after which reaction was again completed in 5 min.

Similar results were obtained after treating the reaction bulb with potassium chloride. At 280°C and 300 mm of each gas, the induction period lasted more than five hours. At 270°C (10°C lower) 20 mm of acetaldehyde again caused inflammation. With 5 or 10 mm of acetaldehyde, there was a 1- to 2-min induction period followed by quiet reaction.

These results are evidently quite different from those obtained by Bone with formaldehyde and methane-oxygen, or acetaldehyde and ethane-oxygen. The induction period is not eliminated by aldehyde but only shortened, unless sufficient aldehyde is present to induce explosion, quite possibly as a purely thermal effect.

The writer inclines to the belief that the effect of acetaldehyde in this case is exerted on the surface. Since altering the surface (coating with potassium chloride) profoundly alters the induction period, the process of "getting-ready" (Bone) is clearly a surface process, as others have remarked. Since this process is only altered but not eliminated by acetaldehyde, this alteration should

likewise be localized at the surface. The nature of the process in the presence or absence of aldehyde is by no means clear, but something in the nature of activated adsorption would seem to be indicated. Alternatively one may be dealing with the slow displacement of a catalyst poison—water vapor, for example. In any case, there is certainly no evidence that aldehyde plays a primary role in the over-all reaction, whatever may be the case in methane or ethane oxidation.

Reaction Period

As already mentioned, these experiments were originally undertaken to obtain further information about the kinetics of propane oxidation subsequent to the induction period. Previous experiments^{4,8,6} had emphasized the "all-or-nothing" character of the reaction (due to the disparity between the lengths of the induction and reaction periods); and had stressed the formation of methanol and formaldehyde with excess of propane, the induced dissociation of the hydrocarbon at higher temperatures, and the unimportance of "active" oxygen in view of the disappearance of peroxides when the reaction bulb was treated with potassium chloride. As to the latter, it had been indicated that the presence of the salt did not materially decrease the over-all reaction rate, as had been the case in the methane-oxygen and hydrogen-oxygen reactions.^{7,5} In view of the elimination of peroxide by this treatment and the repressive influence of packing, it appeared that some effect should be observed. This point was therefore especially investigated. Some suppression by coating does in fact occur, as will later appear.

Experiments Before Coating

The first experiments were conducted with a clean Pyrex bulb 2.5 cm in diameter and 18 cm long. This was rinsed with nitric acid and water before being sealed in place. The bulb was heated electrically, temperature being controlled manually within 1°C, and read on a mercury thermometer graduated in half-degrees. The propane and oxygen (tank gases) were measured into a mixing bulb, and thence passed to the reaction tube. The acetaldehyde was vaporized into the evacuated reaction bulb up to the desired pressure before the reactants were run in. The reaction bulb was adequately but not exhaustively evacuated after each run by means of a Langmuir pump connected to a liquid air trap and Hyvac pump. The exit tube from the reaction bulb was heated by a resistance winding to prevent condensation.

As already mentioned, with 300 mm of each

TABLE I
Reaction at 270°C (5 mm of acetaldehyde)

Uncoated bulb

	Initial pressure in millimeters			
	202	211	205	407
C ₃ H ₈	199	197	384	203
O ₂		202		
N ₂				

Time	Pressure rise			
min	mm	mm	mm	mm
1	0	0	0	1
2	0	0	0	2
3	1	1	1	6
4	2	3	2	14
5	4	5	3	28
6	7	9	6	57
7	12	15	10	63
8	19	22	17	64
9	27	30	26	
10	36	41	34	
11	45	51	45	
12	55	59	55	
13	60	60	63	
14	61		72	
15			79	
20			103	
25			118	
30			119	

gas at 280°C (no acetaldehyde) there was a 40-min induction period followed by a 5-min reaction period.

A preliminary attempt was made to cut the induction period by addition of 10 mm of ethylene oxide to the reactants (300 mm of each). This was ineffective. The pressure rose 5 mm in the first 29 min, after which a further rise of 102 mm completed the reaction in 5 min more. In another run, 25 mm of ethylene oxide was allowed to remain in the reaction bulb 23 min, after which the reactants were added. This was somewhat more effective. The pressure rose 4 mm in 11 min, after which a rise of 101 mm completed the reaction in another 5 min.

Since the induction period was more effectively eliminated with acetaldehyde, this was used in all subsequent runs.

A series of experiments with 5 mm of acetaldehyde as "primer" was carried out at 270°C. Results appear in Table I.

There is an experiment with approximately

TABLE II

Comparison of runs before and after coating
Temperature, 270°C; 5 mm of acetaldehyde added

Initial pressure in millimeters		Time in minutes*	
C ₃ H ₈	O ₂	Before	After
400	200	1	3
200	400	2	22

* This is the time required for the pressure to rise from 20 to 40 mm above the initial value.

200 mm of each gas; the same with 200 mm of nitrogen added; an experiment with 200 mm of propane and 400 mm of oxygen; and one with 400 mm of propane and 200 mm of oxygen. The parallelism among the first three with the same initial propane concentration is obvious. All three accelerate to nearly the same degree up to about 60 mm pressure increase, at which point all the oxygen in the first two is consumed. (On the basis of previous work two volumes of oxygen react with one of propane.) Evidently neither excess of oxygen nor the presence of nitrogen affects this acceleration. This indicates that the rate is really independent of oxygen concentration, and that diffusion to the walls is not a factor. The rate is, however, strongly dependent on the propane concentration.

Experiments After Coating with Potassium Chloride

Following the experiments just described, the reaction bulb was dismantled and filled with dilute potassium chloride solution. After standing several days, it was thoroughly drained and then slowly dried with gentle heating and suction. There was no visible coating on the bulb, but subsequent experiments showed a marked change in activity. The induction period (300 mm of each gas at 280°C with no acetaldehyde) rose from 40 min to over five hours. Addition of acetaldehyde shortened the induction period, but the subsequent reaction was still slower than before coating, as shown in Table III.

A set of experiments corresponding to those made before coating was carried out. In order to keep the induction and reaction periods within reasonable bounds, the temperature was raised from 270° to 280°C and it was found advisable to use 10 mm of acetaldehyde as "primer." Results appear in Table III.

It is evident that the coating of potassium

chloride has completely changed the relationships. Addition of nitrogen now very materially increases the rate, as does an excess of oxygen, once the long induction period has terminated. This rather clearly indicates the importance of diffusion in the coated bulb. The same no doubt applies in part to the marked increase in rate produced by excess of propane.

Discussion

These results have materially altered the writer's conclusions about the nature of the slow

TABLE III

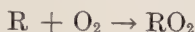
Reaction at 280°C (10 mm of acetaldehyde) after coating with potassium chloride

C ₃ H ₈	Initial pressure in millimeters				
	195	215	213	408	295*
O ₂	196	198	406	204	289
N ₂		204			

Time	Pressure rise				
	mm	mm	mm	mm	mm
1	0	1	0	1	0
2	0	4	1	4	0
3	1	5	1	12	1
4	2	6	1	26	1
5	2	8	1	49	1
6	3	10	1	56	2
7	3	13	1	57	2
8	3	15	1		3
9	4	18	2		4
10	4	22	2		5
11	5	26	2		7
12	5	30	3		10
13	5	35	3		14
14	6	40	3		19
15	6	45	4		26
16	7	50	4		36
17	7	55	4		48
18	7	59	5		63
19	8	60	5		77
20	8	60	6		87
30	14		10		87
40	20		17		
50	27		34		
60	38		63		
70	49		90		
80	56		103		
90	57		112		

* In this run with approximately 300 mm of each gas, only 5 mm of acetaldehyde was added.

oxidation of the higher paraffins. It appears that the destructive action of potassium chloride-treated walls on peroxides is more important than previously concluded.^{4,8,6} The flow experiments at 300°–400°C and 1 atm. had indicated that there was no accompanying change in rate. It is now evident that the rate does not decrease rather markedly under conditions favoring destruction of peroxides at the treated wall. One may therefore conclude that peroxides do in fact play an essential role in the case of the higher paraffins, whatever may be the fact for methane and ethane. It is to be emphasized that the peroxides in question are not of the peracid type, as shown by the analytical evidence^{4,8,6} and by the relative ineffectiveness of acetaldehyde as a "primer." Beyond this their nature cannot at present be specified. The writer naturally is inclined to believe that the reaction



is involved, as suggested by von Elbe and Lewis.⁹ This was previously avoided because of the supposed unimportance of peroxides. However, if one may argue from the slow but persistent increase in rate, sometimes nearly to the very end of

reaction, a more stable intermediate would seem to be required. Possibly the transient compound RO_2 is stabilized by formaldehyde (which is present) to give a hydroxi-peroxide, also suggested by von Elbe and Lewis. For the rest the scheme of the latter authors seems fairly well to exhaust the possibilities.

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Discussion

BERNARD LEWIS and GUENTHER VON ELBE [Published by permission of the Director, U.S. Bureau of Mines, and the Director, Coal Research Laboratory, Carnegie Institute of Technology]: Dr. Pease has brought out some rather striking new facts. At 270°C in an uncoated vessel the reaction rate of propane oxidation was found to be very little accelerated by the addition of nitrogen. After coating the wall with potassium chloride the reaction rate dropped sharply, and in order not to make the experiments unduly tedious the temperature had to be raised to 280°C and a larger amount of acetaldehyde added. Now the rate proved to be strongly accelerated by nitrogen. The substitution of nitrogen by oxygen showed no comparable effect. It is possible to advance an explanation consistent with a branched-chain mechanism such as has been proposed by the writers [*J. Am. Chem. Soc.* *59*, 976 (1937)] in conjunction with the diffusion theory of chain reactions [von Elbe and Lewis: *J. Am. Chem. Soc.* *59*, 970 (1937)] for the case of chain breaking at the wall.

For low chain-breaking efficiency of the wall, the diffusion theory demands that the reaction be independent of the presence of inert gas. For high chain-breaking efficiency, such as may be supposed to exist in potassium chloride-coated vessels, the reaction rate will be much smaller and it will be accelerated by inert gas.

The fact that oxygen does not produce an effect comparable to that of nitrogen suggests that it

should not be regarded only as an inert gas. It may be possible to connect this effect with the inhibition by oxygen of the methyl alcohol-forming chain reaction discovered by Pease [*J. Am. Chem. Soc.* *57*, 2296 (1935)]. We proposed this inhibition [*J. Am. Chem. Soc.* *59*, 976 (1937)] to consist of the oxidation of the chain carrier CH_3O to CO , H_2O , and OH . There are now two principal chain carriers, namely, CH_3O and OH , the former being predominant at high percentages of hydrocarbon and the latter at high percentages of oxygen. It is possible that CH_3O is a more efficient promotor of the reaction than OH , either because it is destroyed at the wall at a smaller rate or because of its greater reactivity in the gas phase, or both.

We have expressed the view that the wall plays the dual role of initiating and destroying chains, the chain-initiating reaction to consist of the dissociation of peracids formed heterogeneously from aldehydes. Such a view would appear to be consistent with experimental facts concerning aldehyde oxidation brought out by Pease and others. It would imply that potassium chloride not only increases the chain-breaking efficiency of the wall but also decreases the rate of chain initiation by the destruction of peracids. The peracids formed in the chain-initiating process are of necessity short-lived at the high temperatures in question, as is also shown by the analytical results in studies of the high-temperature oxidation of aldehydes; in any case they would be present in very small concentrations.

OBSERVATIONS ON THE OXIDATION OF PROPANE

E. J. HARRIS AND A. EGERTON

*Department of Chemical Technology, Imperial College of Science and Technology,
South Kensington, London, England*

Analyses of the products of the slow combustion of propane in oxygen by flow and static methods have been made.

Peroxides are found only when the surface does not destroy them too fast to prevent their detection. In the vapor state hydrogen peroxide appears to be mainly present and dihydroxymethyl peroxide in the condensate.

Propylene is formed early in the reaction, possibly from the aldehydes which initiate the reaction.

Methyl alcohol and aldehydes appear to be formed by the same chain process.

As a result of an investigation carried out on the effect of antiknocks on the combustion of hydrocarbons, Egerton and Gates² concluded that a product of the oxidation of the aldehydes formed in the oxidation of the hydrocarbon assisted the autoxidation of the aldehyde stage of the combustion as well as the initial stage. The effect of inhibitors in delaying the combustion and Semenoff's work⁷ on the oxidation of phosphorus led to the view that the combustion of hydrocarbons took place by a chain reaction mechanism.¹ A study of the oxidation of pentane⁶ helped to confirm this view.

Many investigations have been carried out in order to elucidate the nature of the mechanism of hydrocarbon combustion, but precise knowledge is still lacking. The observations on the oxidation of propane which follow, though they do not purport to do more than indicate some features of the combustion, add a few further facts to those already gathered, particularly by Pease in his studies of the oxidation of this hydrocarbon.⁵

There is a general similarity in the combustion behavior of the straight-chain paraffin hydrocarbons and even of the olefins, which makes it probable that the propagation of the chain is effected in a similar way for different hydrocarbons, excepting that the mechanism in the higher ignition ranges is different in certain respects from that in the lower ranges.

Experiments have been made by the flow method and by the usual "static" method in which the gas mixture is maintained in a vessel at constant temperature. The surface conditions were varied, and small quantities of compounds which may be intermediates in the reactions were added in some of the experiments. The results are in general agreement with those obtained by Pease, but the analyses indicate that hydrogen peroxide is formed, as well as probably a small quantity of acetyl peroxide. Dihydroxymethyl peroxide is present in the condensate formed from formaldehyde and hydrogen perox-

ide. The amount of peroxide found depends on the surfaces to which the vapor is exposed.

Flow System

A measured volume of gas (usually 600 cc) was drawn at a constant rate through a reaction vessel (10 cm long and 1.1 cm in diameter) maintained at a constant temperature. A tube projected into a trap cooled to -40°C at the exit end of the reaction vessel. The gas then passed through a water scrubber into an aspirator; a second tube containing 2,4-dinitrophenylhydrazine sulfate could be used to test whether the absorption of the aldehyde was complete. The volume of gas and weight of condensate were ascertained.

Static System

The silica reaction vessel (A) (42 cm long \times 1.4 cm in diameter) was connected at one end to a gas buret (B) and at the other to a manometer (C) and T-tube (D). The vessel could be connected either to a Hyvac pump or to a trap (E) for condensation of the liquid products, the gas being sucked into a second gas buret (F) by a Toepler pump arrangement (G). In order to obtain sufficient condensate six separate charges of gas were allowed to react to as nearly as possible the same extent as measured by the pressure change. Any aldehyde escaping the trap was collected in a small quantity of water in the gas buret (F). (See Fig. 1.)

Analyses were made, for peroxide by the iodine method using ammonium molybdate as catalyst, for total aldehydes by titrating the alkaline solution before and after oxidation with hydrogen peroxide solution, and for formaldehyde by the mercuric chloride method after distillation to remove alcohols. Ethyl and methyl alcohols were determined in this distillate by oxidation by dichromate.⁸ The amount of higher alcohol was

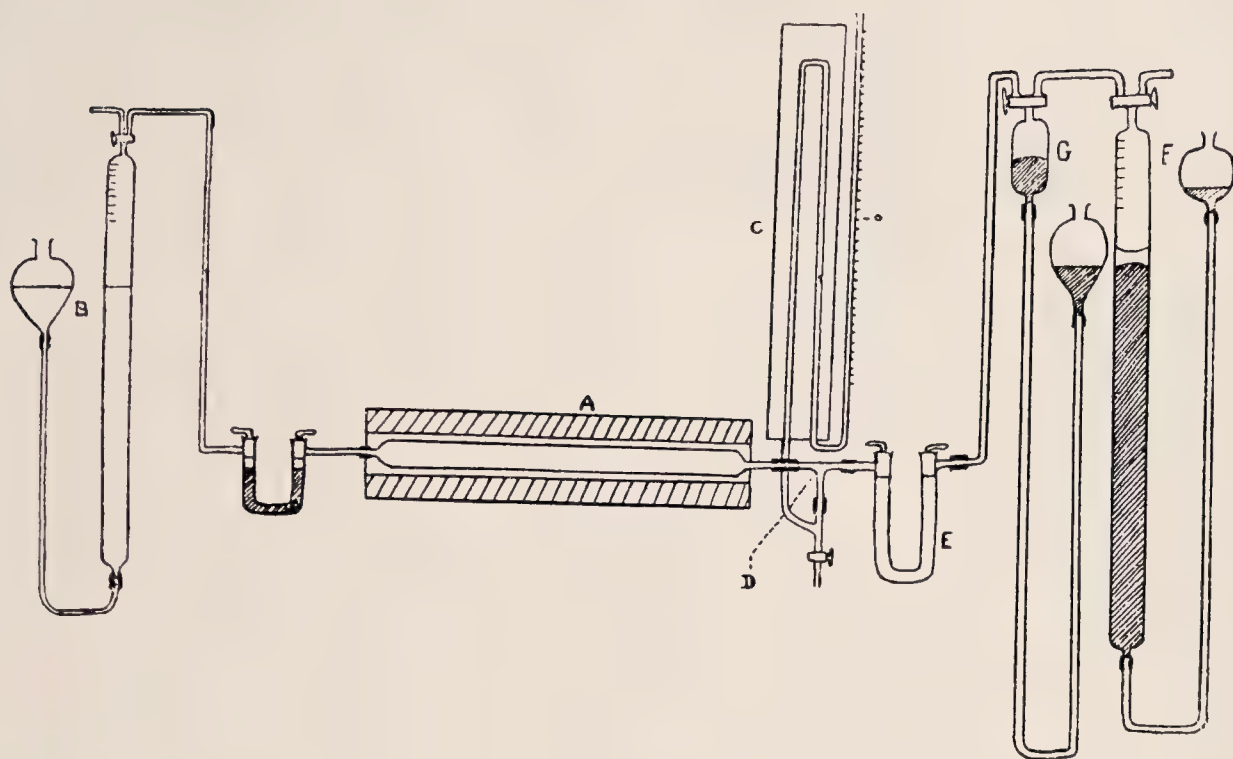


FIG. 1. Static system

found to be small, so that little error was introduced if it was all assumed to be ethyl alcohol. The gas analysis was carried out in a Bone-Newitt apparatus with the addition of a tube of palladinized asbestos for the hydrogen determination.

Static Method Results

The results shown in Table I were obtained using a clean silica vessel washed with hydrofluoric acid, and the same vessel after washing with saturated solutions of potassium chloride and of sodium chloride, respectively. The reactions were allowed to go to completion. It was found that the induction period in successive experiments in the coated tubes became less, reaching a minimum, indicating that products which can initiate reaction are absorbed from the products of the previous run.

The temperature made no appreciable difference in the final composition of the products; it affected, however, the start and the time of the reaction, a higher temperature being needed to start the reaction in the case of the alkali-treated surfaces. The slower reactions were associated with a slightly higher amount of carbon dioxide, due probably to surface oxidation of aldehyde. There is throughout a close correspondence between the amount of oxygen used and the water formed.

The total aldehydes and alcohols were present

in about the same amounts, along with nearly as much unsaturateds which were proved to contain both propylene and ethylene.

Flow Experiments

The yields of products obtained are similar to those of the static experiments, provided the reaction is completed in the time of passage through the tube. The variation in contact time once the induction and reaction period has been exceeded has very little effect.

The peroxides, noted by Pease in the flow experiments, are not obtained in the static experiments, but they are obtained by the flow method using a clean acid-washed silica tube. The yield of peroxide is very susceptible to "poison"; it falls off after a few experiments but the surface can be cleaned again by acid wash. No peroxide is formed if soda glass reaction tubes are used, though Pyrex glass, as used by Pease, was found to behave similarly to quartz. If the hot gaseous products of reaction are led through a soft glass tube, the peroxides are immediately destroyed; so in the static experiments no peroxides were found, though they can be found if the whole reaction vessel is plunged into cold water before removal of the products. These results show that peroxides can be formed, but can only remain in the products if the surfaces to which the gases are exposed do not destroy them.

TABLE I
Results obtained by static method
For 1:1 mixture at 1 atm initial pressure

Vessel	Tempera- ture in °C	Used		Products in gram-moles × 10 ⁻⁴									
		C ₃ H ₈	O ₂	CO ₂	CO	C _n H _{2n}	H ₂	CH ₄	HCHO	RCHO	CH ₃ OH	C ₂ H ₅ OH	H ₂ O
Silica (washed)	322	25	47.4	5.3	28.2	2.8	0.8	6.9	3.7	2.0	8.0	0	41
Silica (KCl)	351	21.8	43.9	5.5	23	4	0.7	4	2.6	3.4	6.4	0	40.5
Silica (KCl)	337	22.8	46	7.8	25.2	4.6	0.6	4.4	2.8	3.2	6.7	0	39
Silica (NaCl)	323-338	24.8	45.7	7.7	19.6	3.6	1.4	6.4	4.1	0.7	3.6	1.8	46
Silica (NaCl)	351	23.1	42.3	6.0	22.6	5.3	0.3	3.4	2.8	2.2	4.1	1.6	39
Silica (NaCl)	351	23.1	42.5	5.7	21.4	4.6	0.9	4.9	2.5	2.9	3.1	0.8	41
Silica (Fe ₂ O ₃)	355	12.4	28.4	8.9	10.7	1.3	0.3	4.0	0	2.3	0	0	25
Graphite tube	320	6.7	20.5	11.5	5.2	0.6	1.0	3.9	0	2.5	1.6	0	9

The peroxide-containing condensate from a prolonged flow experiment was fractionally distilled *in vacuo* at 2.2 cm pressure. The distillate proved to be mainly aqueous methyl alcohol. Decomposition of the peroxides occurred during distillation; in Experiment 1 the amount of peroxide estimated as hydrogen peroxide was approximately 10 per cent of the total liquid before distillation. On rapid distillation violent explosion occurred.

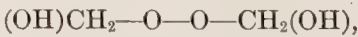
Table II gives the analysis per gram of the products. The quantity of formaldehyde and aldehydes includes the corresponding acids which may be present, though no acid was found in the distillate; the amounts were determined by oxidation of the aldehydes after titration for

TABLE II

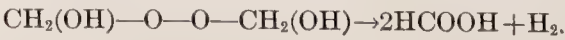
Products	Experi- ment 1	Experiment 2	
	Residue at 40°C	Distillate, 1/3 of the volume	Residue, 2/3 of the volume at 54°C
CH ₃ OH	Trace	0.300	Trace
HCHO	0.309	0.016	0.045
CH ₃ CHO	?	0.076	0.085
Oxygen for acid	?	0.000	0.037
Peroxide as H ₂ O	0.180	0.004	0.022
Total	0.489	0.396	0.193
H ₂ O	0.511	0.604	0.807

acid, the oxygen equivalent to the acid being thus obtained. Peroxides are present other than peroxides which give rise to acid on decomposition. The acidity is appreciable only when large amounts of peroxide are formed and is not equivalent to the total peroxide.

The dihydroxyperoxide



obtained by Lenher⁴ during the oxidation of ethylene, is no doubt present. The ratio of formaldehyde to hydrogen peroxide in the residue in Experiment 1 above is 0.0103 gram-mole/0.0053 gram-mole or 2/1. The behavior with potassium iodide is suggestive of this compound, but also alkaline decomposition of the peroxide condensate yielded a gas containing 80 per cent hydrogen and 20 per cent oxygen, the hydrogen being formed according to the reaction



This peroxide, which is appreciably dissociated at room temperature, is formed from formaldehyde and hydrogen peroxide and probably does not exist in the uncondensed state. This is borne out by the observation that the hydrogen content of the vapors containing peroxide from the flow experiments is not increased by passage through a soda glass tube. The evidence points to hydrogen peroxide and acetyl peroxide being formed, both of which can decompose in the vapor state to give products which are not acid, though the latter may under certain circumstances give rise to acetic acid. There is no evidence for the formation of alkyl peroxides which on decomposition would give rise to further aldehyde or alcohol, unless in too small a quantity to be detected, but their transitory formation and decomposition is possible. (It is noteworthy, however, that in experiments in which ethyl hydrogen peroxide and acetyl peroxide were injected into an engine cylinder, they were collected again from a sample valve with less decomposition than in the case of hydrogen peroxide.)

The fact that no peroxide is formed from coated tubes is no evidence that peroxide-forming radicals are not present during the reaction; it merely means that the surface destroys such peroxide as is formed. The fact that there is little difference in the aldehydes formed in the coated tubes as compared with uncoated tubes indicates

that hydrogen peroxide is the main peroxide existing in the vapor, but this is contrary to Pease's conclusion.

The figures for silica coated with iron oxide show an abnormal amount of carbon dioxide and no alcohols or formaldehyde. Experiments carried out in iron vessels will not be likely to give results similar to those found in glass or silica vessels, surface reaction of the products being enhanced. A graphite tube was also used with somewhat similar results.

Table III gives the amount of the various constituents of 1 g of liquid condensate from flow and static experiments. The results indicate that except for a small variable amount of acids, the presence or not of peroxide makes little difference in the amounts of other products formed.

In the study of the effect of surfaces on the reaction, flow experiments are subject to the difficulty that if the induction period is long no appreciable reaction occurs, whereas if the flow is decreased or the temperature raised sufficiently to start the reaction, the reaction is quickly completed and it is not easy to get reliable analyses of the products before the completion of the reaction. The difficulty is greater because, when once started, the presence of reaction products tends to diminish the induction period.

In static experiments, on the other hand, although they provide means of obtaining analysis

TABLE III

Constituents of 1 g of liquid condensate from flow and static experiments

Peroxide calculated as H ₂ O ₂	Constituents in gram-moles $\times 10^{-4}$					Per cent H ₂ in gas	Conditions	Tem- pera- ture in °C
	H ₂ O by differ- ence	CH ₃ OH C ₂ H ₅ OH	HCHO HCOOH	CH ₃ CHO CH ₃ COOH	HCOOH CH ₃ COOOH			
22.7	300	54.6	38.4	19.4	6.2	1.5	Flow system	335
27.5	349	40.4	33	21.4	9.8	2.3	Silica	
17.5	(385)	26.3	31.5	23.4	8.2	1.6		
	375	44	30.7	19.2	0	1.7	Static system	328
	331	64.6	29.9	23.0	(1.3)	1.0	Silica	322
0.2	337	63.4	30.7	31.4	0.7	0.8	Flow system	344
	346	62.2	35	17.9	1.5	0.9	KCl on silica	
	343	51	33.6	27	0	1.2	KCl on glass	358
	332	57.0	23.8	31.0	3.8	0.8	Static system	337
	346	54.6	21.2	29.1	1.7	1.0	KCl on silica	351
	352	52.4	25.7	20.2	3.7	1.8	Static system NaCl on silica	351

TABLE IV

Analyses of products removed at predetermined pressures in a static experiment

Gas used		Products in gram-moles $\times 10^{-4}$ per 10^{-3} gram-moles of C_3H_8 used										Temperature in $^{\circ}C$
C_3H_8	O_2	O_2 (used)	CO_2	CO	C_3H_6	H_2	CH_4	$HCHO$	$RCHO$	CH_3OH	H_2O	
8.1	13.3	16.4	1.0	5.3	2.7	0.6	5.7	0.7	1.0	0.8	17.9	320
14.2	24.0	16.9	1.55	8.4	1.76	0.3	5.3	1.4	1.1	2.4	17.4	325
22.4	39.8	17.8	1.34	9.4	1.83	0.3	1.1	0.9	1.2	2.0	17.4	340
25.0	47.4	18.9	2.1	11.3	1.1	0.3	2.7	1.5	0.8	3.2	16.8	322
25.7*	50.2	19.5	2.3	9.7	0.7	0.3	2.6	1.2	0.6	2.7	18.2	307

* Trace of acetaldehyde added to shorten induction period.

of the products at different stages of the reaction, the state of the surface is not the same throughout because of the changing composition of the gases. Table IV shows some analyses of products removed at predetermined pressures in a static experiment (silica bulb) with a 1:1 mixture at 1 atm initial pressure: (a) The ratio for this 1:1 mixture of the gases O_2 and C_3H_8 used is approximately 2:1, as found by Pease; (b) The carbon monoxide, carbon dioxide, and methyl alcohol increase throughout, being formed as the result of decomposition of products formed by chain reactions; (c) The water, hydrogen, and aldehydes increase linearly with the amount of reaction, being products probably of chain reactions (their percentage remains constant except in the first stages); (d) The propylene and methane appear to be formed early in the reaction; and (e) The ratio of water formed to oxygen used is 1:1. The experiments recorded in Table V show the effect of the composition of the initial mixture at

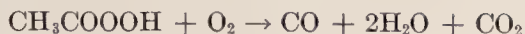
1 atm initial pressure on the composition of the products: (a) The ratio of water formed to oxygen used remains at about 1:1; (b) The ratio of oxygen to propane used, however, changes from 2:1 for the 1:1 initial mixture to 1:1 for the 4:1 initial mixture, the difference between the 1:1 and the 2:1 mixtures being much greater than for the 2:1 and 4:1 mixtures; and (c) The main difference between the 1:1 and the 2:1 mixtures is in the carbon monoxide and water formed. These results indicate that the oxygen in the 1:1 mixture, owing to its higher concentration, provides an intermediate product which directly forms carbon monoxide and water, and about 6 moles more oxygen are consumed per 10 moles of propane reacting than for the 2:1 mixture (four oxygen atoms to carbon monoxide, seven to water, and about two to carbon dioxide). The excess of oxygen in the latter case and in the 4:1 mixture is insufficient to permit appreciable further reaction to carbon monoxide and water.

TABLE V

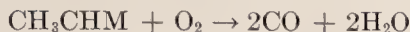
Effect of composition of the initial mixture at 1 atm initial pressure on the composition of the products

Initial mixture C ₃ H ₈ :O ₂	Products in gram-moles × 10 ⁻⁴ per 10 ⁻³ gram-moles of C ₃ H ₈ used										Tempera- ture in °C
	O ₂ (used)	CO ₂	CO	C ₃ H ₆	H ₂	CH ₄	HCHO	CH ₃ CHO	CH ₃ OH	H ₂ O	
1:1	18.9	2.1	11.3	1.1	0.3	2.76	1.48	0.80	3.2	16.8	323
	17.8	1.34	9.4	1.83	0.3	1.12	0.9	1.16	2.0	17.4	340
	18.7	1.9	10.6	1.1	0.2	2.0	1.5	0.95	2.1	18.5	326
2:1	11.4	0.7	6.3	1.74	0.3	3.6	1.1	1.35	1.70	11.1	340
	12.8	1.25	6.8	2.0	0.3	3.0	2.17	0.96	2.66	10.6	340
4:1	10.7	0.68	5.3	2.38	0.7	2.8	1.81	0.96	1.81	10.2	331

It may be that reactions such as



and



break the chains or destroy products, thus accounting for the fact that a large excess of oxygen tends to inhibit the slow reaction.

In the initial stages of the oxidation, the increase in the number of molecules caused by the reaction of one propane molecule is less than in the later stages, probably owing to dissociation of the reaction products; pressure-time curves would need therefore to be corrected before direct deductions about the kinetics of the reaction could be made from them (see Table VI).

TABLE VI

C_3H_8 used	O_2 used	Percentage pressure increase	Percentage increase in C_3H_8 used	Percentage increase in O_2 used
8.1	13.3	4.5	0.56	0.34
14.2	24	7.9	0.56	0.34
22.7	41.1	17.3	0.76	0.42
22.4	39.8	17.2	0.77	0.42
25	47.4	19.8	0.79	0.42
26.3	49.2	21.45	0.82	0.43

The effect of the addition of certain individual reaction products to the initial 1:1 mixture at 300°–340C° was as follows: formaldehyde increased the induction period; acetaldehyde greatly decreased the induction period and increased the yield of methyl alcohol; propylene decreased the induction period; methyl alcohol had no effect.

These and other experiments which are being made at high and low pressures by a variety of methods are part of an extensive investigation of hydrocarbon combustion which is being carried out in the Department of Chemical Technology at South Kensington. Until some of this other experimental work is more advanced, it is not proposed to discuss the above results in detail.

Several schemes to describe the behavior of hydrocarbons on oxidation have been suggested recently: e.g., Norrish's oxygen atom chain, Pease's "methoxyl radical" chain, the "peroxide radical" chain elaborated by Ubbelohde, and a combination and extension of these presented still more recently by Lewis and von Elbe. It is not

TABLE VII

Effect of oxygen concentration on the final amount of propylene

Initial ratio of propane to oxygen	Unsaturateds in gram-moles $\times 10^{-4}$	Surface condition
4:1	4.2	Silica
2:1	4.4	Silica
2:1	4.8	Silica
1:1	4.1	Silica
1:1	4.3	Silica
1:1	4.6	NaCl coated
1:1	4.0	KCl coated
1:1	3.6	NaCl coated
1:1	4.6	KCl coated

Fast
351°C;
slow
330°C

intended to elaborate any further schemes; a true interpretation will probably be found within the range of suggestions which have been put forward, but the experimental facts must be established before a satisfactory theory can be developed. The knocking characteristics of hydrocarbons early convinced one of the authors³ that organic peroxides were playing a part in the oxidation of hydrocarbons. Particularly does that seem to be so now that those characteristics are linked by the work of Townend and his collaborators with the pressure ignition characteristics, but experimental elucidation of their exact function is still lacking. Experimental data are still needed to decide exactly what occurs under different conditions. It must also be pointed out that what happens in one part of the mixture undergoing reaction may be very different from the average behavior of the mixture, so that deductions from kinetics may be sometimes misleading; an exaggerated illustration of this is to be found in the pulsation phenomena of cool flames.

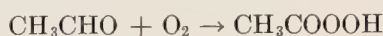
TABLE VIII

Effect of addition of propylene upon final concentration of unsaturateds

Propylene added in gram-moles $\times 10^{-4}$	Unsaturateds in final gas in gram- moles $\times 10^{-4}$
0	4.4
3.6	3.9
7.6	4.3

The oxidation of propane is characterized by (a) initiation by aldehyde, (b) early appearance of unsaturateds (propylene and ethylene), (c) formation of methyl alcohol and total aldehydes in approximately equivalent amounts, (d) destruction of peroxides at surfaces with apparently little change in the composition of the final products, and (e) formation of water approximately equivalent to the oxygen used.

A certain concentration of aldehyde or aldehyde peroxide is needed before reaction starts. It is possible that during this period the following reactions may take place:



As both the formation and oxidation of the propylene depend on the oxygen concentration, the final amount obtained is approximately the same, unless the time during which the propylene is exposed to oxidation is exceptionally long, as Table VII shows.

When propylene is added to a 1:1 mixture of propane and oxygen, the final concentration of unsaturateds obtained is approximately constant, as shown in Table VIII. The fact, therefore, that the concentration of propylene is greater at an early stage of the reaction and is not dependent on the propane concentration seems to indicate that its formation is associated with the products

which initiate the reaction rather than with a direct process of dissociation of the propane. The total aldehydes formed in the reaction are approximately the same in amount as the methyl alcohol, when the oxygen concentration is low so that further oxidation is avoided. This indicates that both methyl alcohol and aldehyde are formed, probably as the products of a reaction chain. On further oxidation the acetaldehyde is burnt preferentially to formaldehyde, giving rise to cool flames; at higher temperatures the acetaldehyde probably dissociates to methane and carbon monoxide. At high pressures other alcohols are known to be formed, and it is probable that other reaction mechanisms come into play.

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THE OXIDATION OF HYDROCARBONS AT HIGH PRESSURE

D. M. NEWITT

Imperial College of Science and Technology, South Kensington, London, England

It is the purpose of this paper to give an account of the effect of pressure upon the formation and survival of oxygenated products during the slow (isothermal) combustion of hydrocarbons in air or oxygen at high pressures, and also to consider briefly the bearing of the results upon the theory of hydrocarbon combustion generally. The data available are unfortunately by no means as comprehensive as could be desired, but sufficient work has been done to leave no doubt but that pressure plays an important part in changing or modifying the course of oxidation during both slow and explosive combustion.

The Role of Pressure

It will be of interest to consider first the possible ways in which pressure may influence the course of a gaseous reaction. One of the direct consequences of raising the pressure is to increase proportionately the frequency of molecular collision; in so far as reaction velocity depends upon collision rate, it will undergo a corresponding increase with pressure. It is, therefore, frequently possible, by suitably increasing the pressure, to carry out a reaction at a temperature considerably lower than would be practicable under atmospheric conditions and by so doing to favor the survival of intermediate products which at higher temperatures would undergo rapid further oxidation or thermal decomposition.

Pressure may also modify the course of a reaction proceeding by a chain mechanism by deactivating the carriers and thus interrupting the chain. Furthermore, a sufficiently high pressure may, by forcing the molecules into close contact, produce such an alteration in their electrostatic fields as to give rise to induced or polarity. Lastly, pressure will influence a reversible reaction in accordance with the Le Chatelier principle of mobile equilibrium in the direction resulting in a diminution of specific volume or molecular density. Examples of all these effects are found in combustion reactions although, owing to their complex character, it is not always possible to account for the results on a quantitative basis.

Apparatus and Experimental Methods

In carrying out pressure oxidations in a small scale plant it is usually not practicable to make provision for adequate heat exchange, and in

order to ensure substantially isothermal conditions the reacting medium must be diluted with a large excess of the combustible or with an inert gas or vapor such as nitrogen or steam; even in a large scale plant it is found advantageous to work with weak mixtures containing not more than 10 to 15 per cent of oxygen.

Two methods have been generally employed, namely: (1) a static method in which a known quantity of the reactants is admitted into a heated reaction vessel and the progress of the reaction followed by the changes in pressure or composition of the medium; and (2) a flow method in which the reactants are passed at a measured velocity through a heated reaction vessel and the products are collected and analyzed.

Figure 1 shows diagrammatically an apparatus suitable for static experiments at pressures up to several hundred atmospheres. The previously mixed hydrocarbon and air or oxygen are compressed into the two steel cylinders A and B to a pressure considerably above the proposed working value, and in the case of the higher hydrocarbons the cylinders are maintained at a temperature sufficiently high to prevent any condensation taking place. The gases pass from the cylinders through the control valve C and the inlet valve I to the reaction vessel F, which is electrically heated. The inlet valve is closed, and after a time interval sufficient for the reaction to take place the contents of the vessel are released through the exit valve J and allowed to pass through a system of condensers K and absorber L, in which condensable and soluble products are removed, to a calibrated gas holder. The initial pressure of the reacting medium is measured by the Bourdon gauge D and its temperature by a platinum-rhodium thermocouple situated in a steel tube traversing axially the reaction chamber.

For the flow method a more elaborate apparatus is required, one form of which is shown in Fig. 2. A and B are storage cylinders containing the reactants at a suitable high pressure. From the cylinders they pass through separate pipe lines to the preheaters C and D and thence through orifice meters E and F to the premixing chamber H. From H they travel directly into the reaction chamber, which is electrically heated, and on emerging are rapidly cooled in the coil K; the condensable and soluble products are removed in the receivers L and M. The residual gases are then reduced to atmospheric pressure by the valve V and are passed through a meter R to a calibrated gas holder. Various adaptations

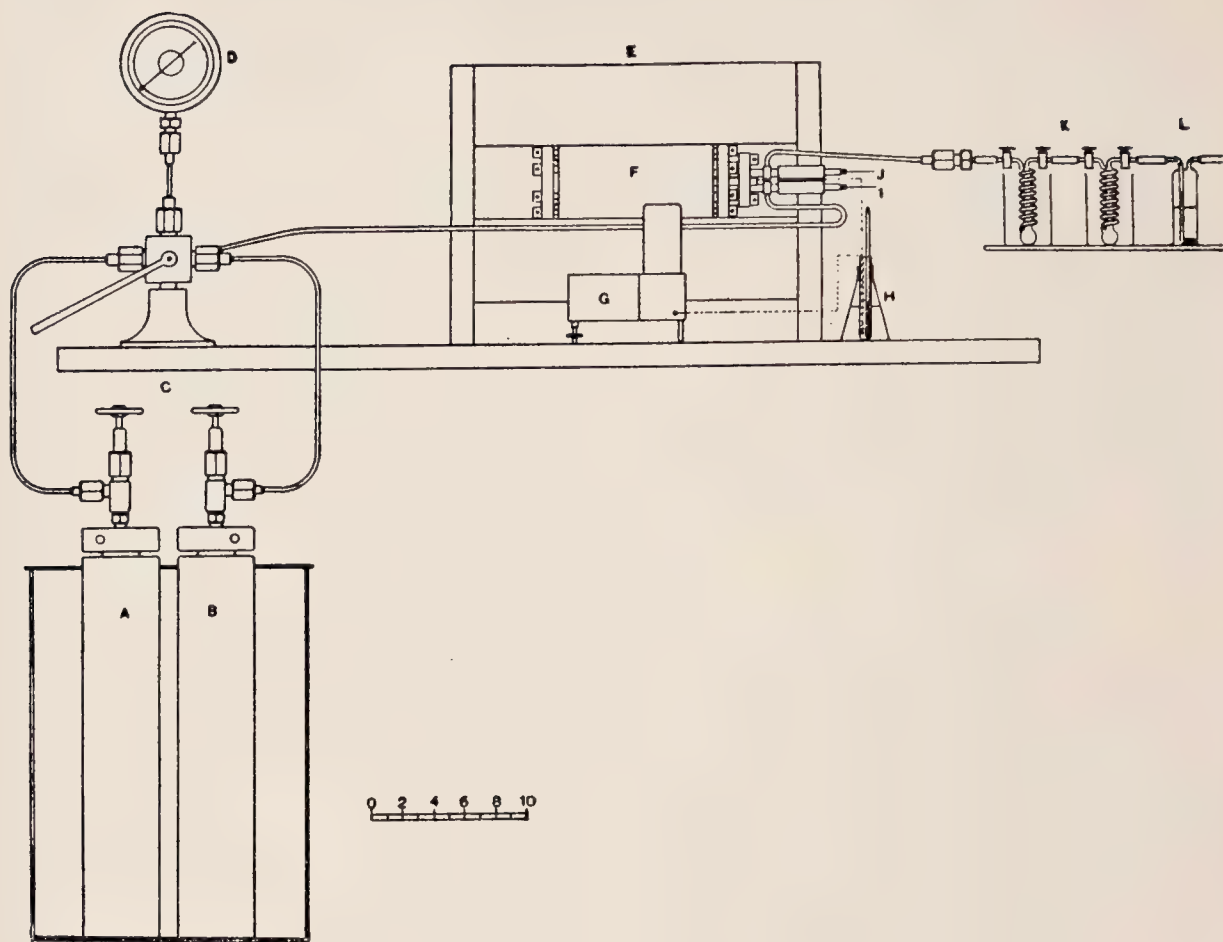


FIG. 1. Apparatus for the static method.

and modifications of this apparatus can be used according to the nature of the investigation.

Of the two methods the static permits of more accurate control of experimental conditions, while the flow method enables larger amounts of material to be used and thus facilitates analyses of the complex mixtures of alcohols, aldehydes, and acids that are found in the products.

Oxidation of Methane

General Characteristics of the High-Pressure Reaction. When a methane-oxygen mixture containing a large excess of the combustible or of an inert gas (e.g., $8\text{CH}_4 + \text{O}_2$) is maintained at a suitable temperature for slow reaction ultimately to take place there is an "induction" period which

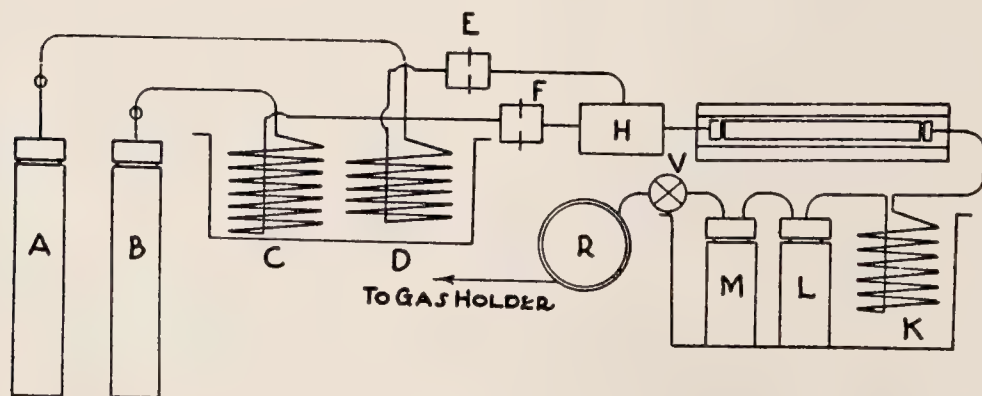


FIG. 2. Apparatus for the flow method.

TABLE I

Products from the slow combustion of an 8.1CH₄ + O₂ medium at 106.4 atm (Ref. 5)

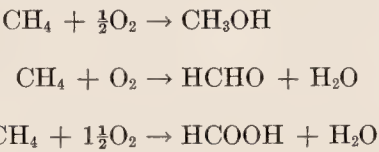
Initial temper- ature, °C	Rise in temper- ature ,°C	Duration of		Products as per cent of methane burnt		Ratio CO/CO ₂ in gaseous products
		Induction, min	Reaction, min	CH ₃ OH	HCHO	
336	4	53	35	10.1	0.30	0.05
339	10	14	22	14.1	0.36	0.01
341	14	2.5	9.5	22.3	0.75	1.5
343	10		12	20.0	0.93	1.0
347	17	2.5	5.5	16.6	0.30	
352	26*	1	1	9.8	0.95	3.9
355	37*	0†	1	3.8	Trace	4.2

* Probable formation of flame during combustion.
† Comparable with time for filling reaction vessel.

may last many minutes, during which little or no oxidation takes place, followed by a reaction period during which the whole of the free oxygen is consumed and various intermediates and end products are formed. The temperature at which reaction first becomes noticeable is found to depend *inter alia* upon mixture composition and pressure; thus an 8CH₄ + O₂ medium will react at comparable rates under the following conditions⁵:

Temperature in °C	Pressure in atmospheres
410	1
360	48
340	105
337	150

The products of the combustion are methyl alcohol, formaldehyde, formic acid, the two oxides of carbon, and steam; hydrogen is found only in exceptional circumstances when the reaction is of an explosive character. The stoichiometric equations for the formation of these compounds, namely,



indicate that while formaldehyde is formed with no change in volume, both methyl alcohol and formic acid result in a contraction. The propor-

TABLE II

The influence of pressure upon the survival of methyl alcohol and formaldehyde in the slow combustion of an 8.1CH₄ + O₂ medium (Ref. 5)

Initial pressure, atm	Initial temperature °C	Duration of oxidation, min	Products as per cent of methane burnt		ratio CO/CO ₂
			CH ₃ OH	HCHO	
10	400	10	1.1	Trace	0.06
25	385	7	4.8	0.66	0.15
40*	372	15	6.1	1.20	0.05
48	373	4	13.7	0.80	0.35
106.4	341	12	22.3	0.75	
149*	341	16	19.0	0.60	0.08

* Not quite optimum conditions.

TABLE III

The influence of diluents upon the yields of methyl alcohol and formaldehyde from the combustion of a $2\text{CH}_4 + \text{O}_2$ medium at 50 atm. pressure (Ref. 5)

Initial mixture $2\text{CH}_4 + \text{O}_2 +$	Temperature, °C	Time of reaction, min	Products surviving, in cc at N.T.P.	
			CH_3OH	HCHO
6.5 N_2	397	16	48	2.7
6.5 H_2O	400	2	43	1.6
6.5 CO_2	390	8	50	3.0
6.5 CH_4	397	1	80	4.6

tions in which they survive depend largely upon experimental conditions and in particular upon temperature and pressure. In a static system, for example, the yields recorded in Table I were obtained for an $8.1\text{CH}_4 + \text{O}_2$ medium at 106.4 atm. and various temperatures between 336° and 355°C.

The data in Table I show clearly that at constant pressure there is an optimum temperature or rate of reaction for the survival of both alcohol and aldehyde, which is probably determined by their respective rates of formation and further oxidation. It is also noticeable that at the higher temperature, when reaction takes place rapidly with a comparatively large temperature rise, the yields of intermediates are considerably reduced, whilst the CO/CO_2 ratio increases.

The effect of increasing the initial pressure is to increase progressively the quantities of alcohol surviving in the products, providing always that the reaction temperatures are so adjusted as to give comparable conditions in respect of reaction velocities. Formaldehyde, which is only found in small quantities, shows little response to pressure (see Table II).

The oxidation proceeds in a similar way when air is substituted for oxygen or when the medium is diluted with nitrogen, carbon dioxide, or steam, but in all such cases the reaction is slowed up and the yields of alcohol are diminished (Table III).

Oxidation of Ethane

Ethane oxidizes rather more readily than does methane, but in other respects the characteristics of its combustion are similar; in both cases the most reactive mixture is one containing the hydrocarbon and oxygen in the ratio 2:1. The products from its slow combustion at high pressures are ethyl and methyl alcohols, acetaldehyde, formaldehyde, acetic and formic acids, the two oxides of carbon, methane, and steam.³ The

proportion in which the carbon of the ethane burnt is distributed amongst these products depends upon the experimental conditions; thus, for example, in the case of an $8\text{C}_2\text{H}_6 + \text{O}_2$ medium reacting on a static system at 50 atm the relative yields are as shown in Table IV.

The results indicate that insofar as ethyl alcohol and acetaldehyde are concerned a temperature giving a medium rate of reaction is most favorable to their survival; acetic acid on the other hand requires a very slow reaction rate, while methyl alcohol varies little throughout the series.

The effect of increasing the pressure is favorable to these products containing two carbon atoms but reduces the yields of methyl alcohol and formaldehyde (see Table V).

From the point of view of the mechanism of hydrocarbon combustion it is important to know something of the order in which the various intermediates are formed and to distinguish between those participating in the main reaction and those resulting from secondary reactions. Some light is thrown on this matter by the results of experiments carried out by the flow method⁹; if, for example, a hydrocarbon-oxygen mixture is passed through a heated zone at progressively increasing velocity, then, provided the products are rapidly chilled, those initially formed should survive in increasing amounts. In this way it has been shown that at high pressures methyl and ethyl alcohols are formed at an early stage in the oxidation of methane and ethane, respectively.⁷ Furthermore, when methyl and ethyl alcohols are themselves oxidized at high pressures the products include all those found in comparable reactions with the parent hydrocarbons (Table VI).

Oxidation of Propane

Propane occupies a very important position between the lower and higher members of the paraffin series, for while its properties show

TABLE IV
Products from the reaction of an $8C_2H_6 + O_2$ medium at 50 atm and various temperatures

Duration of		Percentage of the carbon of the ethane burnt surviving as											
Initial tempera- ture, °C	Induction, Reaction,		C ₂ H ₅ OH	CH ₃ OH	CH ₃ CHO	HCHO	CH ₃ COOH	HCOOH	CO	CO ₂	CH ₄	Total liquid products	Total gaseous products
	min	min											
279.2	18.0	100.0	14.8	10.8	4.7	0.2	15.2	0.3	19.3	32.5	Nil	46.0	51.8
286.0	7.0	3.8	24.4	14.1	8.3	2.0	1.7	0.9	34.8	10.0	Nil	51.4	44.8
288.0	6.5	3.8	20.5	11.3	7.3	1.2	2.3	0.7	31.6	7.1	13.7	43.2	52.4
289.0	4.2	2.8	16.0	14.4	4.9	2.0	2.4	0.4	36.0	4.6	20.7	40.1	61.3
294.0	2.0	3.2	17.2	14.1	5.2	1.9	Nil	0.7	40.8	7.8	8.1	39.1	56.1

TABLE V
The influence of initial pressure on the survival of intermediate products from the reaction of an $8C_2H_6 + O_2$ medium

Percentage of the carbon of the ethane burnt surviving as										Total condensable products
Initial pressure atm	Initial temperature, °C	Duration of reaction, min	C_2H_6OH	CH_3OH	CH_3CHO	$HCHO$	CH_3COOH	$HCOOH$	CH_4	
15	315	3.0	16.0	19.4	1.9	4.5	Nil	Nil	Nil	41.8
50	294	3.25	17.2	14.1	5.2	1.9	Nil	0.7	0.7	39.1
75	279	2.5	18.0	16.6	6.8	0.4	3.6	0.6	0.6	46.0
100	270.5	4.5	23.6	14.0	9.7	0.1	12.5	0.5	0.5	50.4

TABLE VI
Products from the slow oxidation of ethyl alcohol at 100 atm and 261° C

Partial pressure of reactants in atmospheres		Initial tem- perature, °C	Products as percentage of the alcohol oxidized or decomposed							
C ₂ H ₅ OH	O ₂		CH ₃ CHO	CH ₃ COOH	CH ₃ COOC ₂ H ₅	CH ₃ OH	HCHO	HCOOH	CO ₂	CO
20	4	261	32.8	0.8	39.9	7.5		0.5	5.1	13.6
20	10	261	20.7	2.4	36.2	13.5	0.2	0.3	20.4	3.6
10	10	261	10.4	1.4	35.6	8.2		0.4	27.6	12.5
5	10	261	3.4	1.7	19.4	4.3	Trace	0.3	63.0	7.9

certain resemblances to those of methane and ethane its reaction with oxygen is characterized by features peculiar to the higher hydrocarbons. The work of Prettre¹⁰ and of Beatty and Edgar¹ has shown that during its slow combustion luminescence may be observed and in certain circumstances cool flames may be formed, while Townend and Chamberlain¹² have mapped out its upper and lower regions of inflammability.

The Reaction at High Pressures. When propane is oxidized at high pressures the products contain not only most of those intermediate substances found in the low-pressure reaction—namely, propyl, ethyl, and methyl alcohols, propion-aldehyde, acetaldehyde, and formaldehyde, and propionic, acetic, and formic acids—but also isopropyl alcohol and acetone arising probably from some initial oxidation at the center —CH₂ group.⁶ The role of pressure in inducing such a change in the primary process is by no means clear, but evidence suggests that it may be due to a change in polarity of the hydrocarbon molecule altering the ratio of the collision period leading to activation and the vibrational periods of the C—C or C—H linkages.

The effect of a progressive increase of pressure upon the distribution of products is well brought out by the data summarized in Table VII, which relate to the reaction of a 1:3.6 propane-air

TABLE VII
Products from the reaction of a 1:3.6 propane-air medium at 1, 20, 60, and 100 atm

Products	Pressure, atm			
	1	20	60	100
	Reaction temperature, °C			
	373	281	252	250
Percentages of the carbon of the propane burnt				
A { Total aldehydes	20.5	21.8	13.5	13.7
{ Normal alcohols	19.7	21.0	17.5	15.2
B { Isopropyl alcohol	1.3	2.8	6.2	16.0
{ Acetone	0.5	4.3	12.5	7.9
Acids	4.3	17.0	19.0	18.9
Carbon dioxide	7.3	17.1	21.4	20.6
Carbon monoxide	21.3	16.0	9.9	7.7
Propylene	25.1	Nil	Nil	Nil
Ratio A/B	22.3	6.0	1.7	1.2

TABLE VIII

Products from the reaction of various propane-air mixtures at 30 atm pressure and 275°C

Products	Propane:air ratio				
	1:20	1:5	1:3.6	1:1.25	1:0.5
Percentages of the carbon of the propane burnt					
A { Total aldehydes	12.5	8.8	12.0	16.1	16.7
A { Normal alcohols	17.3	25.5	23.0	33.1	34.5
B { Isopropyl alcohol	2.7	6.9	5.2	5.2	14.4
B { Acetone	1.2	1.4	1.3	0.3	7.4
Acids	13.9	13.4	15.2	8.9	12.5
Carbon dioxide	31.5	25.0	22.1	10.5	7.0
Carbon monoxide	20.9	19.0	21.3	25.9	8.0
Total condensable products	47.6	56.0	56.7	63.6	85.5
Ratio A/B	7.6	4.1	5.4	9.0	2.4

medium at four pressures in the range 1 to 100 atm.

The most noticeable feature of these results is the absence of peroxidic bodies and of propylene in the high-pressure experiments and the increasing amount of isopropyl alcohol and acetone surviving as the pressure increases. If the sum of the total aldehydes and normal alcohols, A, and of the isopropyl alcohol and acetone, B, be taken as a rough measure of the tendency for oxidation to take place at a terminal methyl group and the central $-\text{CH}_2$ group, then the progressive decrease in the ratio A/B indicates that the latter process is favored by pressure.

It has been shown that in the case of methane and ethane an increase in the concentration of the hydrocarbon favors the survival of liquid products, and propane behaves in a similar manner. Thus when a series of propane-air mixtures in which the proportion of propane is varied from 1:20 to 1:0.5 react at 30 atm pressure and 275°C in a static system, the results given in Table VIII are obtained. The total condensable products increase from 47.6 per cent for a 1:20 mixture to 85.5 per cent for a 1:0.5 mixture.

The Distribution of Alcohols. The normal alcohols formed during the slow combustion consist of methyl, ethyl, and propyl alcohols, methyl alcohol usually being present in excess (Pease⁸); the proportions in which they survive, however, depend upon the pressure, increasing amounts of propyl alcohol being found at the higher pressures. Thus, for example, Wiezevich and Frolich find that for an 11:1 propane-oxygen mixture, reacting at 170 atm and 350°C, methyl, ethyl, and

propyl alcohols are found in the approximate ratio 13.4:8:5.2, while Newitt and Schmidt⁶ working with a propane-air mixture at pressures between 5 and 65 atm. obtained the data given in Table IX.

The formation of a series of normal alcohols from propane suggests that initial oxidation occurs at an end methyl group giving propyl alcohol, which then undergoes further oxidation *via* propionaldehyde to give in turn ethyl and methyl alcohols. In support of this view is the fact that propyl alcohol on oxidation at 240°C and 56 atm yields propionaldehyde, acetaldehyde, ethyl alcohol, and propionic and acetic acids, while ethyl alcohol at 280°C and 50 atm gives acetaldehyde, methyl alcohol, and acetic and formic acids. Propyl and ethyl alcohols are, however, more easily oxidized than is methyl alcohol, and consequently the latter would be expected

TABLE IX

Relative quantities of alcohols surviving from the slow reaction of a 1:3.6 propane-air medium

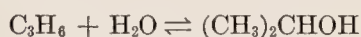
Products	Pressure, atm			
	5	30	65	
Methyl alcohol, %	76.3	58.0	55.3	50.1
Ethyl alcohol, %	19.1	17.6	13.2	9.8
Propyl alcohol, %	4.6	4.3	7.3	12.2
Isopropyl alcohol, %		20.0	24.2	27.9

TABLE X
Products obtained in high-pressure
oxidation of butane

Inlet oxygen going to:	Per cent of oxygen at	
	33 atm	133 atm
Acetone	1.4	0.7
Methyl alcohol	15.0	8.4
Ethyl alcohol	2.5	6.3
Propyl alcohols	3.2	8.9
Butyl alcohols	0.6	2.5
Aldehydes	6.9	15.9
Acids	16.7	4.6
Carbon dioxide	9.4	6.1
Carbon monoxide	3.8	9.4

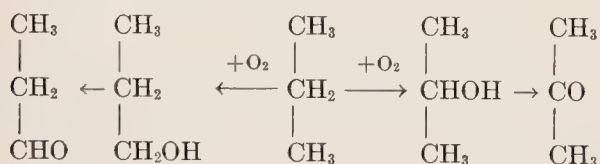
to, and in fact does, survive in large quantities in the product.

The increasing amounts of isopropyl alcohol and acetone found in the products as the combustion pressure is raised have been attributed to oxidation at the $-\text{CH}_2$ group. An alternative view is that isopropyl alcohol might arise from hydration of propylene which occurs in large quantities during the low-pressure combustion. The reaction



however, requires the presence of a catalyst and the value of its equilibrium constant at 300°C indicates that a considerable amount of propylene should be present in the system at equilibrium, whereas it is almost entirely absent in the high-pressure experiment.

It may therefore be concluded that the propane molecule can undergo oxidation in two ways according to the following scheme,



the proportions in which the oxygen is distributed depending upon the temperature, pressure, and the concentration of the reactants.

Oxidation of Butane

The products from the high-pressure oxidation of butane are too complex to admit of accurate quantitative analysis. Wiezevich and Frolich¹⁴ have, however, identified acetaldehyde, propionaldehyde, acetone, acetic acid, propyl acetate, and methyl, ethyl, isopropyl, *n*-propyl, and isobutyl

alcohols and give the data presented in Table X to show the effect of pressure upon the types of products produced. Low pressure tends to favor the formation of lower alcohols and acids, and high pressure the formation of higher alcohols and aldehydes. The data are not sufficiently detailed to afford any indication as to the point of initial oxygen attack, although the presence of isobutyl alcohol shows that some oxidation takes place at the $-\text{CH}_2$ groups.

Oxidation of the Aromatic Hydrocarbons

Although the controlled slow oxidation of the aromatic hydrocarbons forms the basis of a number of industrial processes such as, for example, the production of phthalic acid from naphthalene and of maleic acid from benzene, the actual mechanism by which ring cleavage occurs is still a matter of surmise. By carrying out such oxidations in the vapor phase at high pressure,⁴ however, comparatively low reaction temperatures can be employed and enhanced yields obtained of those nuclear derivatives formed in the primary processes before the ring breaks; in this way the successive steps in the initial phase of the oxidation of benzene, toluene, and ethylbenzene have been identified.

Benzene. The principal products from the oxidation of an excess benzene-oxygen medium in a static system at pressures of the order of 50 atm are phenol, the two oxides of carbon, and steam. Smaller quantities of hydroquinone, quinone, maleic acid, and formaldehyde are also found, together with biphenyl, arising from the direct pyrolysis of the benzene. Unlike the reaction in the case of the aliphatic hydrocarbons, that of benzene is not preceded by any marked induction period and cool flames are not observed.

The yields of phenol from experiments at 312°C with a series of mixtures in which the

TABLE XI
Oxidation of a 4:1 mixture of benzene and air at
50 atm and 362°C

Products	Percentage distribution of oxygen
Phenol	10.6
Hydroquinone and quinone	Trace
Maleic acid	2.8
Formaldehyde	3.0
Carbon monoxide	26.2
Carbon dioxide	29.8
Water	27.6

TABLE XII

Products from the reaction of various toluene-oxygen mixtures at 20 atm

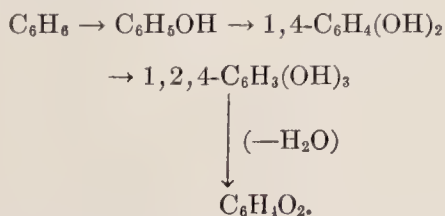
Initial mixture $\text{C}_6\text{H}_5\text{CH}_3 : \text{O}_2$	Reaction temperature, °C	Products as percentages of the carbon of the toluene burnt						Percentage distribution of oxygen in	
		Benzyl alcohol	Benzaldehyde	Benzoic acid	2, 4-Dihydroxytoluene	CO_2	CO	Side chain	Nucleus
30*	337	6.2	50.6	16.3	9.9	5.2	5.4	81.5	18.5
20*	276	5.9	36.1	12.1	14.7	3.0	1.4	71.0	29.0
3.7	250	2.8	21.9	26.2	6.1	17.9	6.0	86.5	13.5
3.2	250	1.6	18.1	53.0	6.3	18.3	4.7	91.0	9.0
1.5	250	1.2	8.6	47.1	5.1	19.6	3.3	91.0	9.0
1.0	250	0.7	3.0	59.3	7.1	25.8	3.8	89.5	10.5

* These mixtures contained 3.76 atm of nitrogen.

benzene-oxygen ratio was varied between 20:1 and 1.9:1, the partial pressure of the hydrocarbon being kept constant at 20 atm, are⁴:

Ratio $\text{C}_6\text{H}_6 : \text{O}_2$	Per cent of the C_6H_6 burnt surviving as phenol
1.9	12.8
3.7	37.7
9.9	24.9
20.0	38.3

It is clear that an excess of the hydrocarbon is favorable to the survival of phenol. Similar results are obtained with benzene-air media, the products from a 4:1 mixture at 50 atm and 362°C being as given in Table XI. The phenol recovered from this experiment represents upwards of 50 per cent of the benzene burnt. It is noteworthy that aromatic products other than phenol seldom survive in anything but traces in the homogeneous vapor-phase reaction; nevertheless the presence of hydroquinone and quinone¹³ is significant in that it affords evidence that oxidation of the nucleus proceeds by successive stages of hydroxylation, as represented by the following scheme:



Toluene and Ethylbenzene. The products of the oxidation of the simple alkyl derivatives of benzene may be divided into three groups, according as they result from oxidation of the

nucleus, of the side chain, or of the fragments resulting from ring cleavage. The relative proportions in which each group survives depend *inter alia* upon temperature, pressure, and mixture composition. In the case of toluene the principal products are: (1) From side-chain oxidations (benzyl alcohol, benzaldehyde, and benzoic acid); (2) from nuclear oxidation (*p*-cresol and 2,4-dihydroxytoluene); (3) from ring cleavage (aliphatic acids, formaldehyde, the two oxides of carbon, and steam.) In addition bibenzyl is formed by the pyrolysis of toluene and small quantities of benzene from the decarboxylation of benzoic acid.⁴

The proportions in which the more important of these substances are found in the products from a series of toluene-oxygen mixtures at 20 atm reacting in a static system are shown by the results in Table XII. It is evident that the course of the combustion and particularly the extent to which the side chain undergoes oxidation are influenced to a very marked degree by the composition of the medium. Thus while the comparatively rich 1:1 toluene-oxygen mixture gave 59.3 per cent of benzoic acid in the products and only 3 per cent of benzaldehyde and less than 1 per cent of benzyl alcohol, the 30:1 mixture gave 6.2 per cent of benzyl alcohol, 50.6 per cent of benzaldehyde, and only 16.3 per cent of benzoic acid. In the case of the latter mixture no less than 83 per cent of the carbon of the toluene burnt appeared as aromatic intermediates in the products.

The reaction temperature has also a considerable influence upon the distribution of the products, as may be seen from the data in Table XIII, relating to two mixtures containing toluene and air in the proportions of 20:5 and 30:5,

TABLE XIII

Products from the combustion of 20:5 and 30:5 toluene-air mixtures at various temperatures

Temperature, °C	Products as percentages of the carbon of the toluene burnt					
	Benzyl alcohol	Benzaldehyde	Benzoic acid	2, 4-Dihydroxy-toluene	CO ₂	CO
20 C ₆ H ₅ CH ₃ + 5 air						
276	5.9	36.1	12.1	14.7	3.0	1.4
304	5.6	38.6	17.7	15.0	3.5	3.0
331	6.0	40.4	19.4	17.9	4.5	3.8
375	15.8	30.0	10.2		14.4	5.3
400	31.1	30.1	8.1	10.2	14.7	4.2
30 C ₆ H ₅ CH ₃ + 5 air						
337	6.2	50.6	16.3	9.9	5.2	5.4
358	8.3	45.4	10.6	10.7	4.0	5.5
391	16.6	31.0	9.7	9.3	4.2	3.9
503*	6.6	3.2	3.6	3.9	3.5	9.8

* Inflammation occurred with carbon deposition.

respectively, the partial pressure of oxygen being 1 atm. An important feature of these results is the progressive increase in the amount of benzyl alcohol surviving with increase of temperature, together with a corresponding decrease in benzoic acid. It is evident that by suitably adjusting the temperature and the hydrocarbon-oxygen ratio any one of the three side-chain derivatives can be obtained in high yields relative to the amount of hydrocarbon consumed.

Ethylbenzene. In the liquid phase ethylbenzene combines readily with oxygen at temperatures of 100°–120°C giving acetophenone and the oxides of carbon but no alcohol or aldehyde¹¹; in the presence of a manganese oxide catalyst, however, methylphenylcarbinol, benzoic acid, and formaldehyde are found in addition to the above products.² In discussing the mechanism of the reaction Stephens concludes that the hydrogen attached to the carbon atom in the alpha position is first removed and that oxygen tends to substitute in the same position as do the halogens, giving acetophenone; the alcohol is regarded as arising from some independent secondary reaction.

Newitt and Burgoyne, on the other hand, have studied the vapor-phase combustion and show that reaction in these circumstances takes place by successive hydroxylations of the hydrogen attached to the carbon atom in the alpha position, yielding as a primary product methylphenylcarbinol, which in turn gives acetophenone. The further oxidation of acetophenone occurs by

hydroxylation of the hydrogen attached to the carbon in the beta position, giving benzaldehyde and benzoic acid. At the same time some direct oxidation of the nucleus takes place, giving as the main product 2,4-dihydroxyethylbenzene.

As an example of their results the data of Table XIV relating to a 20:7.5 ethylbenzene-air mixture reacting at 27.5 atm and 322°, 385°, and 437°C, respectively, may be given. The increase in the methylphenylcarbinol with increase of reaction temperature affords evidence that it constitutes the initial product of the oxidation. The above experiments also show that with rise

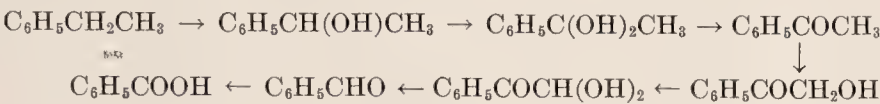
TABLE XIV

Products from the combustion of a 20:7.5 ethylbenzene-air medium at 27.5 atm

Products	Reaction temperature, °C		
	322	285	437
	As percentages of the carbon of the ethylbenzene burnt		
Methylphenylcarbinol	8.9	11.5	27.7
Acetophenone	13.4	Trace	Trace
Benzaldehyde	54.0	52.3	23.6
Benzoic acid	6.4	8.9	8.7
2,4-Dihydroxyethylbenzene	10.3	9.2	6.8

of temperature there is an increasing tendency for the nucleus to undergo direct oxidation, the distribution of oxygen between the side chain and the nucleus at the three temperatures being:

Temperature, °C	Per cent distribution of oxygen in:	
	Side-chain products	Nuclear products
322	77.0	23.0
385	75.0	25.0
437	69.0	31.0



Summary and Conclusions

A general survey of the experimental data relating to the combustion of both the aliphatic and the aromatic hydrocarbons makes it clear that pressure exerts a well-defined influence on the course of the reactions involved. It has been shown in the foregoing pages that it accelerates the rate of reaction, exerts a directive action on the primary oxidation process, and influences to a marked degree the distribution of the oxygen in the products. In all cases of pressure oxidation in which oxygen is in defect the products have been shown to contain large quantities of normal alcohols or phenolic derivatives arising at some early stage of the oxidation. Thus it is possible to burn methane under conditions which give yields of methyl alcohol of upwards of 50 per cent, and similar results are obtained with ethane, propane, benzene, and toluene.

With the higher aliphatic hydrocarbons another pressure effect of importance is the change in the point of oxygen attack on the molecule; there is an increasing tendency with rise of pressure for direct oxidation to occur at some midpoint in the chain giving iso-alcohols and ketones, the change being probably attributable partly to the increase in the collision factor and partly to a change in the polarity of the molecule due to close packing.

The alkyl derivatives of benzene show a somewhat similar behavior, for while the side chains are more open to attack and at atmospheric pressure appropriate all the oxygen, at high pressures the nucleus and side chains undergo simultaneous oxidation.

Without entering into any discussion involving the kinetic aspects of the various oxidations, there is evidence from the analytical results that the initial stages of the process taking place at high pressures are represented by the following

Although the formation of benzaldehyde and benzoic acid has been attributed to further oxidation of acetophenone, they might equally well arise from ethylbenzene by successive hydroxylations of the hydrogen attached to the carbon in the beta position. In this event phenyl-ethylalcohol should be the first step in the oxidation and should be detectable in the products; no trace of it, however, has ever been found, while experiments with acetophenone show that on oxidation considerable amounts of benzaldehyde and benzoic acid are formed. The intermediate stages in the oxidation of ethylbenzene would therefore appear to be:

scheme:

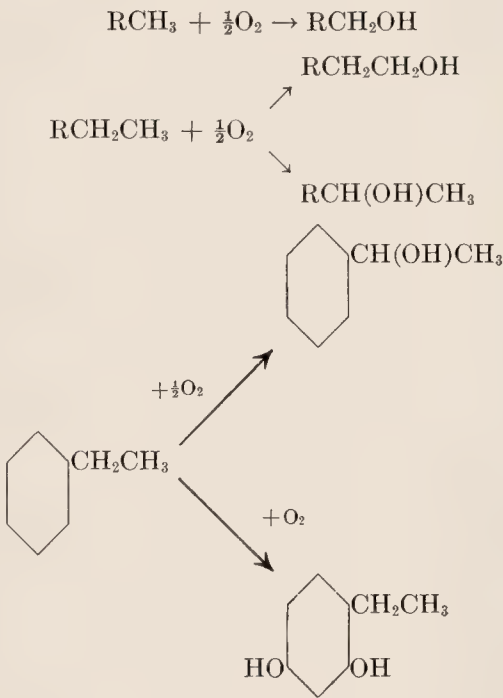


TABLE XV
Effect of pressure upon the rate of reaction

Hydrocarbon	Temperature at which oxidation is first detectable when the pressure is:			
	1 atm	50 atm	100 atm	150 atm
Methane	420	350	330	320
Ethane	285	276	260	
Propane	270	255	245	232
Butane		248	220	210
Benzene		270	260	
Toluene		210	195	

The effect of pressure is generally to increase the rate of reaction, as may be seen from the comparative figures in Table XV.

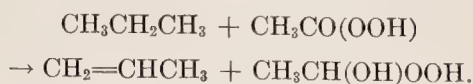
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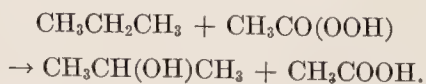
Discussion*

Bernard Lewis and Guenther von Elbe: Dr. Newitt has interpreted his results in terms of initial hydroxylation. It appears to us that a scheme based on a chain mechanism involving chain carriers of the peroxide type would do more justice to his results. This has already been outlined by us in the case of the oxidation of methane and ethane at high pressures [*J. Am. Chem. Soc.* **59**, 976 (1937); *Combustion, Flames and Explosions of Gases*, Cambridge University Press (1938)]. In particular, the radical chain allows a ready interpretation of the yields of methyl and ethyl alcohols in the oxidation of ethane. It is not difficult to account for all the observed products and the trends of their yields with varying temperature, pressure, and mixture composition.

Among his newer results on the oxidation of propane we note, in particular, the simultaneous appearance of isopropyl alcohol, acetone, and acids and the disappearance of propylene and peroxides as the reaction temperature is lowered and the pressure increased. This reaction may be understood from our previously proposed formation of oxy-alkyl peroxides and olefins by reactions between peracids or their radicals and paraffins. At lower temperatures this reaction is easily conceived to take a somewhat different course than at higher temperatures. Thus, at high temperatures the following reaction might be favored:

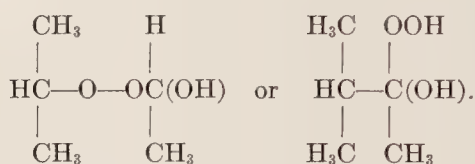


Low temperatures would favor



It is possible that the primary step in the above two reactions is a condensation of the hydrocarbon

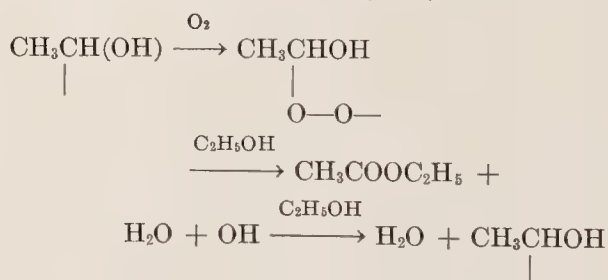
and peracid to form



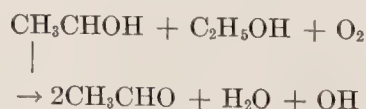
which then split up into the products noted at different temperatures.

The acetone could be formed in a subsequent step from isopropyl alcohol, for example, by a reaction with a peroxide.

Another example that may be mentioned is the oxidation of ethyl alcohol at high pressures. The lower the percentage of oxygen in the mixture, the larger the yields of acetaldehyde. The yield of ethyl acetate, which is one of the main products, is much less susceptible to change in mixture composition. The formation of the latter substance is readily represented by a radical chain, viz.,



If at constant pressure the percentage of oxygen is decreased, the number of binary collisions between alcohol radical and oxygen should decrease relative to the number of ternary collisions



thus leading to larger yields of acetaldehyde.

Regardless of the correctness of these particular schemes, we believe that a consistent interpretation of the oxidation of hydrocarbons is possible only along these lines.

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THE MECHANISM OF THE COMBUSTION OF HYDROCARBONS*

GUENTHER VON ELBE

Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pennsylvania

AND

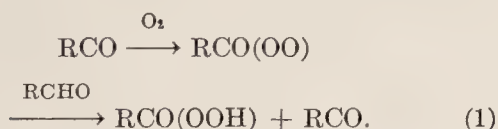
BERNARD LEWIS

Explosives Division, Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pennsylvania

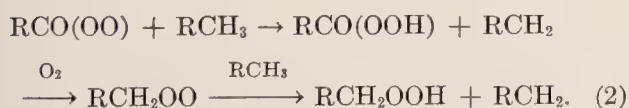
The purpose of this paper is to present a critical comparison of recent theories suggested by Norrish and Foord,⁶ Ubbelohde,¹³ Jost and coworkers,⁴ Pease,⁷ Semenov,¹² and von Elbe and Lewis¹⁴ for the mechanism of the combustion of hydrocarbons. The subject may be divided into the chemical mechanism and the kinetics of the oxidation. A detailed description will not be presented, the object being to discuss viewpoints on subjects touched on by several authors.

The Chemical Mechanism

The Unbranched-Chain Reaction. It is generally agreed that the oxidation of hydrocarbons occurs by a chain mechanism and that aldehydes appear as intermediates. Both Ubbelohde and von Elbe and Lewis formulate the chain reaction on the basis of evidence obtained in the oxidation of aldehydes. The latter reaction is also of the chain type, and it is reasonable to assume that both the above chain reactions are interdependent. Ubbelohde follows Bäckström's¹ mechanism by which the aldehyde oxidation chain is initiated by the formation of a radical RCO which then reacts according to the scheme:



According to Ubbelohde, in the presence of a paraffin hydrocarbon



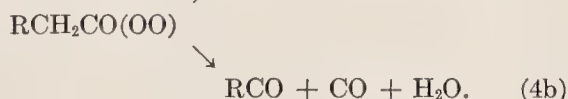
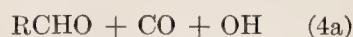
The alkyl peroxide undergoes decomposition



a reaction of which the peroxide radical may also be capable, to give either aldehyde and OH

or aldehyde radical and H₂O. Such suggestions are also advanced by Jost and coworkers. For the formation of the main oxide of carbon, namely carbon monoxide, Ubbelohde, as well as Jost, proposes the subsequent decomposition of the aldehyde formed in Reaction (3), or of the aldehyde radical formed in Reaction (1), leaving the saturated hydrocarbon or hydrocarbon radical, respectively. As a side reaction, Ubbelohde proposes the occasional transformation of the hydrocarbon radical into olefin and hydrogen atom; this, however, is a strongly endothermic process. Having shown experimentally the formation of oxygen ring compounds in the higher paraffin series, he arrives at a simple mechanism for such ring formation from peroxide radicals. Furthermore, the formation of alcohols at high pressures is accounted for by the interaction of two peroxide radicals to yield two molecules of alcohol and O₂.

von Elbe and Lewis arrive at Bäckström's mechanism [Reaction (1)] from the following independent evidence. In the photochemical decomposition of aldehydes, monovalent radicals are formed; in the photo-oxidation of aldehydes higher than formaldehyde, peracids are formed by a chain mechanism. These two facts alone make Reaction (1) the only plausible one, and in addition this mechanism correctly describes the dependence of the yield on light intensity and concentrations of reactants. According to von Elbe and Lewis, the decomposition of aldehydes or their radicals into carbon monoxide and hydrocarbon or radical is not plausible. This is shown particularly by the experiments of Pope, Dykstra, and Edgar⁸ on the thermal decomposition of aldehydes. However, it is very plausible that the peracid or its radical should decompose at the high temperature, for example, according to the scheme:

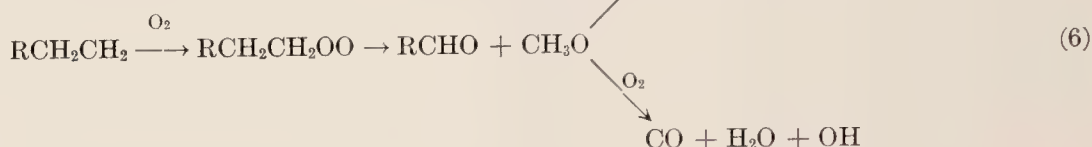
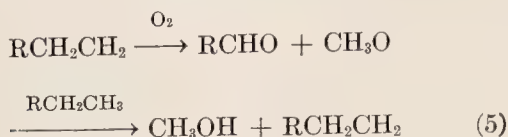


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This would agree with Pope, Dykstra, and Edgar's over-all "degradation" reaction which in normal paraffins ultimately leads to formalde-

hydes and which in isoparaffins is interrupted at the ketone stage.⁹ Various possibilities of this interruption have been discussed by Jost.

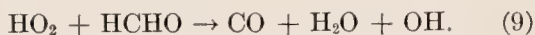
For the oxidation of an alkyl radical, Pease proposed the following chain instead of the second and third steps in Reaction (2),



If the alkyl radical is CH_3 , a direct association with O_2 is very improbable, as is indicated by the work of Kimball.⁵ This also applies to the formaldehyde radical HCO . Therefore, for ordinary pressures, von Elbe and Lewis postulate



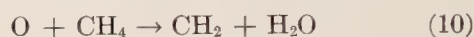
HO_2 reacting according to



In the oxidation of rich mixtures of methane at high pressures CH_3OO may be formed in three-body collisions and give rise to methyl alcohol by various reactions, involving presumably the primary condensation of methyl peroxide or its radical with formaldehyde, followed by dissociation at the peroxidic bond. This corresponds to the peroxide studies of Rieche and coworkers.¹⁰ This hypothesis proves to be fruitful in accounting not only for the experimental facts connected with the high-pressure oxidation of methane and ethane, but also for the low-temperature branching of higher paraffins (see below). In particular, in the high-pressure reaction the effect of mixture composition on the alcohol yields is explained by the susceptibility to oxidation of the alkoxy radical as in Reaction (6). The suggestions of Jost and coworkers concerning alcohol formation at high pressures are not far removed from the above: A ternary collision between alkyl radical, O_2 , and hydrocarbon molecule is postulated to lead either immediately to alcohol and alkoxy or to alkyl peroxide and an alkyl radical, the peroxide to dissociate into OH and alkoxy, the latter giving rise to alcohol.

since he observed the formation of large amounts of methyl alcohol at moderate temperatures in rich mixtures of propane and oxygen. In order to reconcile this mechanism with the probable appearance of alkyl peroxides as proposed by Ubbelohde, which is made plausible by the appearance of a low-temperature branching reaction (see below), and with the absence of methyl alcohol in lean mixtures of propane and oxygen, von Elbe and Lewis introduced the following modification of Reaction (5):

Norrish's chain mechanism is based entirely on the alternate appearance of oxygen atoms and alkylene radicals which, for methane, he writes



and for formaldehyde oxidation as an unspecified chain mechanism involving oxygen atoms. At high pressure, oxygen atoms are assumed to combine with hydrocarbons in a three-body collision to form alcohols. The reaction constitutes a chain-breaking process in the gas phase which is of the first order with respect to the chain carrier. A similar chain-breaking process with monovalent radicals is impossible. A number of objections to the oxygen atom mechanism have been advanced by Ubbelohde, Jost, and von Elbe and Lewis, among which two may be mentioned. If oxygen atoms are introduced into hydrocarbons at room temperatures, emission of the band spectra of C_2 , CH , and OH occurs; that is, radicals appear possessing a different number of free valences than the oxygen atom. In the slow oxidation of methane these spectra are not emitted. Instead there is the fluorescence spectrum that has been found to arise from excited formaldehyde. If oxygen atoms were participating in the mechanism, the absence of bands of C_2 , CH , and OH would be difficult to explain. A second objection is that a reaction between an oxygen atom or a bivalent radical with a saturated molecule can easily be conceived as leading to two monovalent radicals which should exhibit the properties of chain carriers. The reverse process—namely, the formation of bivalent from monovalent radicals—

would require the reaction of two monovalent radicals, which would be a very rare event in view of their low concentration.

The view is generally accepted that at ordinary pressures chains are broken principally at the wall.

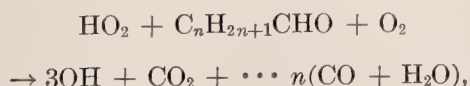
Chain Branching. The low-temperature reactivity and explosivity of higher hydrocarbons can be explained by assuming a branching reaction with an optimum probability in a certain temperature range. Ubbelohde suggests branching to occur on collision of an energy-rich peroxide with hydrocarbon to yield water, alkyl radicals, and alkoxy radicals or to occur in a triple collision between two hydrocarbon molecules and a peroxide radical to yield two alkyl and one alkoxy radicals. Assuming the lifetime of the peroxide molecule or its radical to be limited by the decomposition reaction³ and to be shorter the higher the temperature, branching is favored at lower temperatures. Essentially the same idea is proposed by Jost. On the other hand, von Elbe and Lewis propose a branching reaction which had already successfully accounted for the alcohol yields in the high-pressure reactions and was supported by the chemistry of peroxides. According to this, the breaking of the peroxidic bond is sensitized by the condensation of the peroxide or its radical with aldehyde. This branching mechanism accounts for the influence of aldehyde on the low-temperature explosion peninsula, which is not described by the alternative branching mechanisms of Ubbelohde and Jost. The branching probability is largely determined by the lifetime of the peroxide radical, which is governed by a decomposition reaction analogous to Reaction (3). The absence of a low-temperature explosion peninsula in methane is easily understood by the inability of methyl radicals to form methyl peroxide radicals except in triple collisions. The gradual disappearance of the low-temperature explosion peninsula in higher paraffins having more condensed structures is again connected with their decreasing ability for form aldehydes.

The oxygen atom mechanism of Norrish apparently does not admit a similar set of plausible competing reactions.

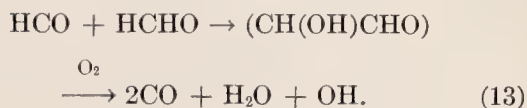
The explosion limit of methane and the high-temperature explosion limits of higher hydrocarbons can be explained, according to von Elbe and Lewis, by another branching reaction:



or



competing with a reaction involving primary formaldehyde condensation, namely,



The necessity for introducing reactions of this kind depends on whether one considers the high-temperature explosion to be of the thermal or branched-chain type. This will be discussed below.

Kinetics

The Steady-State Rate. Detailed kinetic treatments are to be found in the work of Norrish and Foord, which is confined to methane, and in the work of von Elbe and Lewis. Both treatments are based on the production of chain carriers by aldehyde, assumed to be a homogeneous reaction by Norrish and Foord and a heterogeneous reaction by von Elbe and Lewis, and the destruction and production of aldehyde by chain mechanisms. Since in von Elbe and Lewis' treatment the concentration of formaldehyde at the surface is assumed to be proportional to the gas-phase concentration, both mechanisms are kinetically equivalent, except for the homogeneous alcohol-forming chain-breaking reaction of Norrish and the branching reactions of von Elbe and Lewis. For the case of negligible branching and neglecting the alcohol-forming reaction, the steady-state rate following the establishment of the maximum aldehyde concentration is in both cases proportional to the square of the hydrocarbon concentration and the first power of the oxygen concentration. If aldehyde forms chain carriers in the gas phase, then for a chain-breaking efficiency of the wall that is large compared with the ratio of the mean free path to vessel diameter, the reaction rate is proportional to the total pressure and the proportionality factor in the rate equation is independent of the nature of the surface.¹⁵ If the chain-breaking efficiency is small compared with the above ratio, the rate becomes inversely proportional to the chain-breaking efficiency, but the additional pressure factor in the rate equation disappears.¹⁵ In the first of the above cases the rate is proportional to the square of the diameter and in the second case to the first power of the diameter.

If aldehyde forms chain carriers at the wall, no additional pressure factor enters into the rate equation, and the proportionality factor always depends on the nature of the surface.¹⁵ As long as branching is negligible the rate is independent of diameter.

The pronounced effect of surface on the rate

rules out the first case under the formation of chain carriers from aldehyde in the gas phase. Concerning the second case, it is not very probable that vessels having walls of extremely low chain-breaking efficiencies should have been used by all investigators. According to the theory, a decision between the second and third cases (formation of chain carriers from aldehyde at the wall) should be possible by investigating the diameter dependence of the rate. In ethane-oxygen mixtures at low pressures (a few centimeters of mercury) and at about 600°C in silica vessels etched with hydrofluoric acid, the rate has been found to be independent of diameter.¹¹ The experiments were well reproducible, pointing to the conclusion that etching produces a more or less uniform and stable surface. In unetched vessels the results were erratic. Norrish and Foord investigated the effect of diameter on the rate in untreated cylindrical Pyrex vessels at 530°C in the pressure range 150 to 300 mm of mercury. They find a mild diameter dependence between diameters of 7.5 mm to 37.5 mm, although for small vessels they find a sharp drop in the rate. Before any conclusions are drawn from these results, the influence of pressure should be mentioned.

At a constant total pressure of about 1 atm and at 447°C, Bone and Allum² found that a mixture containing 66.7 per cent of methane in oxygen reacted faster than mixtures containing 50 or 75 per cent of methane. At 467°C and at pressures ranging from 300 to 600 mm, Fort and Hinshelwood³ found the rate to depend on a power of the methane concentration exceeding 2 and a power of the oxygen concentration exceeding 1. At 480°C and presumably up to atmospheric pressure, Norrish and Foord found approximate proportionality of the rate to the product $(\text{CH}_4)^2P$ at constant oxygen pressure and to the product $(\text{O}_2)P$ at constant methane pressure. They also added nitrogen to 250 mm of methane and 100 mm of oxygen up to a total pressure of about 800 mm and found approximate proportionality of the rate to total pressure.

Of these results, those of Bone and Allum are most readily interpreted by the fact that the product $(\text{CH}_4)^2(\text{O}_2)$ reaches a maximum at 66.7 per cent methane. The other observations on the influence of total pressure are predicted neither by case 2 nor by case 3 unless one grants that the chain-breaking efficiency of the wall is inversely proportional to the pressure. This is not inconceivable if one considers the possible influence of adsorbed gas layers on the wall. It is also possible that aldehyde produces chain carriers both by a heterogeneous and by a homogeneous reaction with oxygen, the former predominating at lower pressures and the latter at higher pres-

ures. One would then expect some intermediate case between 1 and 3, thus allowing for the influence of the nature of the surface, the diameter dependence, and the pressure factor.

There is still one other possibility which was specifically considered by von Elbe and Lewis,¹⁴ that is, case 3 obtains and chain branching is not negligible. The branching term would introduce a diameter dependence and a pressure factor of variable orders depending on the relative magnitudes of the chain-breaking and chain-branching rates. Experiments have not been sufficiently extensive to rule out the necessity for such flexibility.

Norrish and Foord do not fully apply the diffusion theory, in that they assume the rate of chain breaking always to be proportional to a factor S/Pd , S being the surface activity per unit area, P the total pressure, and d the diameter of the vessel. Therefore they have not fully treated the complex problem of accounting simultaneously for the influence of pressure, diameter, and nature of the surface. Strictly within their own picture, the chain-breaking rate should be proportional to $1/Pd^2$ for efficiencies large compared to the ratio of the mean path to diameter and proportional to S/d for efficiencies small compared to this ratio. In the former, the influence of the nature of the surface would have had to be sacrificed and a fairly powerful diameter dependence introduced; in the latter, the pressure factor would have had to be sacrificed.

The Explosive Reaction. In the treatments of Norrish and Foord and of von Elbe and Lewis aldehyde is both created and destroyed by chain carriers. The rate of production of formaldehyde is at first a very slow process, because the concentration of chain carriers is very small. Its rate of destruction is still smaller, because the aldehyde concentration is also very small. Assuming that the production of new chain carriers by aldehyde is a rare event, one can appreciate the rather long induction periods during which the aldehyde concentration increases, until finally it becomes comparable in magnitude to the concentration of hydrocarbon (of the order of 1 per cent) and the rates of formation and destruction of aldehyde approach equality. The reaction rate then reaches its steady-state value. Norrish and Foord believe that explosion occurs if this maximum rate is sufficiently fast to destroy the thermal equilibrium. They link their theory to the Semenov theory of "degenerate" branching.¹² The latter author's views, however, differ from those of Norrish and Foord and of von Elbe and Lewis in that the intermediate product, which presumably must be identified with aldehyde, is oxidized to the final products inde-

pendently, that is, without reacting with a chain carrier. Thus, if the concentrations of the reactants, hydrocarbon and oxygen, remained constant, there would be a steady accumulation of the intermediate product and consequently a continuous acceleration of the reaction rate due to production of new chain carriers by aldehyde. The rate would never reach a steady state and only exhaustion of the reactants would slow it down. From a chemical point of view, this course of the reaction is hardly conceivable, because it is known that aldehyde is oxidized by a chain reaction. Semenoff's support for his argument, namely, that the inflection point in the rate curve occurs at a high percentage of the total reaction, is not borne out by the experiments of Norrish and Foord. It should also be mentioned that without prejudicing the steady-state theory, a constant reaction rate cannot actually be observed during the course of the reaction because the effect of exhaustion of the reactants should occur early, so that the nonexplosive reaction will always consist of a period of acceleration followed by a period of deceleration.

There remains the question whether the explosion is of the thermal type (Norrish and Foord) or of the branched-chain type (von Elbe and Lewis). There are no certain simple criteria to decide this question. Only the upper explosion limits of such mixtures as hydrogen or carbon monoxide and oxygen can be ascribed, with some assurance, to chain branching. In the present case, thermal and branched-chain theories both demand a continuous acceleration of the reaction on approaching the explosion limit by the change of any experimental variable. It is not justifiable to give preference to either theory from observations of this type, unless the observations can be made accurately and quantitatively and compared with a quantitative theory. Neither theory nor experimental technique has developed to this stage.

Norrish and Foord base their preference for the thermal character of the explosion on their observation that the induction periods, measured in the nonexplosive region up to maximum reaction rate and in the explosive region up to ignition, lie on a continuous curve when plotted against total pressure. However, this result is also consistent with the branched-chain theory.

Although the reaction rate depends rather strongly on the nature of the surface, the branched-chain theory¹⁵ demands that the explosion limit be relatively unaffected by the nature of the surface unless the chain-breaking efficiency is small compared with the ratio of the mean free path to vessel diameter. Actually, the limit is found to be influenced somewhat by the nature of the surface. Assuming that the chain-

breaking efficiency is large compared with the abovementioned ratio, this does not rule out the possibility that the limit is essentially governed by a chain-branching mechanism and that it is lowered somewhat by a thermal factor which enters in by virtue of the acceleration of the reaction rate near the limit.

von Elbe and Lewis base their preference for the branched-chain theory of the explosion on the effect of mixture composition on ignition temperature. Whereas the maximum reaction is at a mixture composition of about 66.7 per cent methane in oxygen, the minimum ignition temperature has been found for a mixture containing about 33 per cent methane. Judging from the change of the product $(\text{CH}_4)^2(\text{O}_2)$ and the change in thermal conductivity of the mixtures, this shift of optimum composition appears entirely too large to be accounted for by the thermal theory in connection with the proposed chain mechanism of the slow reaction, and to require the introduction of an additional mechanism which is readily conceived of as a branching mechanism. The argument is strengthened still further by the effect on the minimum ignition temperature of substituting helium for argon as diluent in methane-oxygen mixtures. Keeping the total pressure constant one would expect, on the basis of the purely thermal theory, the minimum ignition temperature in helium mixtures to shift to a larger ratio of methane to oxygen as compared to argon mixtures, because the larger heat conductivity of the former mixtures would require a faster reaction to destroy the thermal equilibrium. Actually the reverse is true, the minimum ignition temperature in helium mixtures being shifted toward smaller ratios. The branched-chain mechanism as proposed by von Elbe and Lewis accounts for these and related facts.

Summary

Recent theories of hydrocarbon oxidation have been critically compared. The evidence favors monovalent radical chains. The assumption of intermediate formation of peroxides and of sensitization of peroxide dissociation by condensation with aldehyde proves to be fruitful in explaining varied phenomena, such as the low-temperature reactivity of higher hydrocarbons and the high-pressure oxidation of methane and ethane. The implications of the chain theory in interpreting the experimental results have been discussed. The necessity of revising Norrish and Foord's steady-state treatment has been pointed out. The question of thermal versus branched-chain explosions in methane remains open, with some experimental evidence favoring the latter.

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Discussion

Harold A. Beatty (Ethyl Gasoline Corporation, Detroit, Michigan): The pioneer work of Pope, Dykstra, and Edgar [J. Am. Chem. Soc. *51*, 2203 (1929)] on the slow oxidation of branched-chain octanes suggested that a stepwise degradation of the longest straight chain takes place until a secondary carbon atom is reached, at which point a stable ketone is formed. This suggestion has been more or less accepted as a specific fact by subsequent investigators, without its having been put to experimental proof. Actually, the results of some previously unpublished work by the author in 1931 on the slow oxidation of 2,5-dimethylhexane indicate that the over-all reaction is by no means as simple as was originally suggested. Using the conventional flow method [Beatty and Edgar: J. Am. Chem. Soc. *56*, 102 (1934)] it was found that the oxidation of this octane in air starts at a low temperature, 235°C. At 346°C the reaction is very fast, the temperature near the inlet being 74°C above that of the thermally uniform portion of the furnace, 272°C, and it may safely be assumed that 75 to 100 per cent of the hydrocarbon is partially oxidized. Holding this temperature constant, 17.40 g of the hydrocarbon was oxidized in 635 min at a molal oxygen/fuel ratio of 9.6.

Analysis of the gaseous products uncondensed at -78°C gave, per mole of hydrocarbon input, 2.30 moles of oxygen used, and 0.73 mole of carbon monoxide, 0.10 mole of carbon dioxide, and 0.08 mole of unsaturated gas (probably ethylene) formed.

The liquid condensate weighed 23.44 g, giving a total recovery of 99.9 per cent. It contained, per mole of hydrocarbon input, 1.80 moles of water and about 0.2 mole of acid, principally formic acid. So far this is in fairly good agreement with the suggested mechanism of oxidation to 5-methylhexanone-2.

However, the aqueous condensate, $d = 1.05$, weighed 11.4 g of which only 40 per cent was water; aldehyde and acetone were present in quantity. The upper layer, $d = 0.84$, weighing but 12.0 g, had a boiling range from below 90°C to above 155°C. The fraction boiling below 100°C, 3.6 g, gave a strong test with Schiff's reagent, and yielded a *p*-nitrophenylhydrazone melting at 142.5°–143.5°C, with a molecular weight of about 200 to 225, apparently not a single compound. The fraction boiling from 115° to 155°C, 3.1 g, gave negative tests with sodium, sodium bisulfite, and semicarbazide, and a trace of oil with *p*-nitrophenylhydrazine; certainly none of the expected ketone was present.

This analysis is admittedly far from complete, but it serves its purpose to the extent of showing definitely that a certain amount of extensive degradation or rupture of the carbon chain takes place, and that no 5-methylhexanone-2 appears in the products. It seems, therefore, that while the original suggestion is probably valid in principle, it cannot be accepted literally or specifically, and each individual branched-chain hydrocarbon will have to be considered, to a certain extent, as an isolated problem.

THE MECHANISM OF THE COMBUSTION OF HYDROGEN

LOUIS S. KASSEL

Universal Oil Products Company, Chicago, Illinois

Introduction

The combustion of hydrogen, in common with that of the other fuels dealt with in this symposium, may occur either as a slow reaction or as an explosion, depending upon the experimental conditions. This paper treats these two main types of reaction separately. The reaction kinetic interpretation of the foregoing phenomena will constitute the third and final section. The space available does not permit anything like complete discussion of a reaction which even in 1934 could be the subject of a 100-page monograph,¹⁷ and many aspects of the reaction will be omitted entirely.

The Slow Reaction

The reaction between hydrogen and oxygen may be brought about catalytically by a variety of metallic surfaces. These catalytic reactions have been carefully studied in a number of cases, and have given interesting information concerning the relative adsorption of hydrogen, oxygen, and steam on the surfaces involved. The temperature of these reactions is so low, however, that they are almost totally unrelated to the phenomena of combustion as the term is usually understood, and they will therefore not be discussed in the present paper.

A catalytic reaction is found even with ordinary silica or porcelain reaction vessels. This catalysis, however, is far feeblar than that by most metals, the rate being easily measured in a static system at 520°C. This reaction is approximately of the first order with respect to hydrogen, nearly of the zero order with respect to oxygen (except at quite low partial pressures), and retarded by steam. This catalysis can only be observed when the pressure is sufficiently high; at lower pressures there is a more or less instantaneous explosion, the nature of which is dealt with in the following section. When experimentation is confined to pressures above this explosion limit, very striking changes in the reaction kinetics are observed as the temperature is raised. Below about 540°C the reaction is of low order, has a low temperature coefficient, is retarded by steam, and is accelerated in a packed vessel. At slightly higher temperatures the reaction is of high and variable order (about fourth), has a very high temperature coefficient, and is accelerated by steam or other inert gases and retarded in a packed vessel. There is no reason to doubt that the low-temperature surface reaction continues into this range with

the characteristics that would be predicted for it by extrapolation. The changed kinetics are due to a quite new reaction, taking place predominantly in the gas phase, which becomes much faster than the surface reaction. This gas reaction can be studied only for a narrow range of conditions. The pressure must be above the previously mentioned explosion limit, and below a second (or, more precisely, as develops later, a third) limit. These limits come together as the temperature is raised and cut off the non-explosive reaction completely at about 580°C. Below about 550°C, on the other hand, the normal wall reaction is fast enough to obscure or even to obliterate the gas reaction.

The temperature coefficient of the homogeneous reaction increases with increase of both temperature and pressure. Values up to 4.3 for 10°C at 560°C are found, corresponding to an "activation energy" of 200 kg-cal. It will be seen in the third section, however, that there is no physical significance to the energy of activation for reactions of this type.

The gas reaction is of about the third order with respect to hydrogen and the 1.5 order with respect to oxygen.^{16,12} The addition of nitrogen to a stoichiometric mixture increases the initial rate about linearly with the amount added, the increase being roughly the same as would be produced by an equal quantity of oxygen. Other inert gases behave similarly, the relative effectiveness of helium, nitrogen, argon, and water being in the ratio 1:3:4:5.

The rate is very markedly reduced by packing the reaction vessel. The effect of surface is best studied quantitatively, however, by working with cylindrical vessels of equal length but varying diameter. Initial rates for stoichiometric mixtures at 560°C were found as follows¹⁷:

Bulb diameter, mm	Rate at 600 mm	Rate at 300 mm
17	0.85	0.18
32	3.49	0.50
56	9.35	0.94
77	33.8	3.45

These values are roughly proportional to the square of the diameter; the rate at 600 mm in the largest bulb is about double the expected value, presumably because this measurement was made on the borderline of the high-pressure explosion region.

When a silver reaction vessel is used, this homogeneous reaction is not found.¹⁵ There is a slow wall reaction with a rate nearly independent of the hydrogen pressure and unaffected by inert gases. Introduction of a silica rod is without effect. It therefore appears that the reaction chains which leave the silica surface are rapidly destroyed by some action of the silver.

The homogeneous reaction is sensitive to gaseous inhibitors. At 450 mm and 550°C the rate is markedly reduced by the addition of 0.01 mm of chlorine, bromine, or iodine, falling to as little as one-tenth of its original value in the case of iodine.¹⁰ When the quantity of halogen is varied, the rate is found to pass through a minimum and then to increase slowly for larger additions, remaining for a long time less than if no halogen were present. There is good evidence that the increase is due to a wall reaction, one step of which is the known heterogeneous oxidation of the hydrogen halide. The actually observed minimum rate, therefore, does not represent the maximum inhibition of the homogeneous reaction. Since the gas reaction is slower in small reaction vessels, it is not surprising that it should be less susceptible to inhibitors; this is found to be the case.

The Explosion Region

At pressures lower than those of the homogeneous reaction there is a region of more or less instantaneous reaction. This explosion normally takes place only between two well-defined pressure limits, which depend upon the temperature and composition.

Of the two limits, the upper is more easily studied, since the effect there is sufficiently vigorous to be easily noted, and still more since the position of the limit is quite stable. The upper limit is independent of the diameter of the vessel, and is nearly the same in porcelain, silica, and alumina. At constant temperature the limit can be fairly well represented by

$$f_H(H_2) + f_O(O_2) + f_X(X) = \text{const.},$$

where X represents any inert gas and the f_H , f_O , f_X are constants. The constant on the right of the equation increases with temperature at a rate corresponding to an activation energy of about 26 kg-cal.^{25,13,9}

In quartz vessels of moderate size the lower limit is at pressures of the order of 1 mm.²⁵ In the region near the limit the explosions are feeble and correspondingly difficult to detect. The position of the limit is very susceptible to the pretreatment of the surface, and it is for that reason practically impossible to make really

comparable experiments in different vessels. It is at least approximately true, however, that the limit is represented by

$$(H_2)(O_2)d^2 = \text{const.}$$

in the absence of inert gases. In the presence of inert gases the lower limit is lowered, that is, explosion occurs for partial pressures of hydrogen and oxygen which by themselves would be unreactive. The effect of helium is greater than that of argon. It appears to be an unwarranted exaggeration of the experimental accuracy in this difficult region to deduce the functional form of the lower limit taking account of the inert gas effect. The effect of temperature also is rather uncertain. It seems that when the upper and lower limits are far apart, the lower limit decreases only slightly as the temperature is increased, but that for low temperatures, where the two limits come together, the effect is considerably greater.

Within the explosion region ignition is by no means instantaneous. Kowalsky²⁰ used a photographically recorded membrane manometer to follow the course of the reaction at pressures only moderately above the lower limit. The initial parts of his curves show an exponential increase in rate with time, the acceleration being greater the higher the temperature and the greater the pressure excess over the lower limit. The maximum rates were reached at times of the order of 0.1 sec. This "induction period" is thus quite distinct from the very much longer induction periods characteristic of hydrocarbon-oxygen explosions near the lower limit.

The boundaries of the ignition region are profoundly altered by various departures from the "normal" conditions prevailing in quartz vessels. It has already been suggested that the position of the lower limit is sensitive to the condition of the surface. It is not surprising, therefore, that marked changes are produced when totally different surfaces are used. Thus Frost and Alyea,⁹ using potassium chloride-coated Pyrex vessels, found the lower limit at pressures some tenfold higher than other workers report in quartz; the dependence of the limit on concentration is also changed, being given by

$$(O_2)[g_H(H_2) + g_O(O_2) + g_X(X)] = \text{const.}$$

The complete absence of surface produces an equally striking effect. Alyea and Haber¹ found by experiments with crossed streams of separately preheated gases that ignition did not occur at 520°C at pressures of 20–100 mm, well within the ignition region in quartz. The nonigniting gases could be lit by a rod of quartz, glass, porcelain, copper, or iron, but not by one of aluminum. It had previously been shown^{12a} that

ignition took place with crossed streams at 560°C and atmospheric pressure.

When an aluminum vessel is used, the ignition is apparently suppressed, but the presence of a quartz rod restores the normal ignition region. With a silver vessel no ignition could be obtained even at 700°C, and in this case the presence of quartz had no effect.¹⁵ In fact, it was found that even with a quartz vessel ignition was frequently prevented by the presence of silver wires; this result was considered ambiguous, however, since the silver wires used, which were apparently more active catalytically than the surface of the silver reaction vessel, produced sufficient steam to quench the explosion.

The addition of a few hundredths of a per cent of nitrogen dioxide produces a very great broadening of the ignition region, the upper limit being raised and the lower limit lowered, and the minimum ignition temperature reduced to about 350°C.²⁵ For larger additions the limits are narrowed again; as a result, for any fixed mixture and temperature, there are two limiting concentrations of nitrogen dioxide, between which ignition occurs, but beyond which it does not. For constant temperature and composition these limits approach each other as the pressure is raised. For constant pressure and composition they approach as the temperature is lowered. At constant pressure and temperature the upper limit is lowered when the proportion of oxygen is increased, or when nitrogen is added.

Small quantities of halogens affect the ignition in the opposite way, and one part of iodine or bromine in 10,000 suppresses it completely, at least in the normal temperature range. The effect of chlorine is similar but much feebler, 0.25 per cent being required for suppression.¹⁰

Steam has a similar effect, but of quite a different magnitude, 36 per cent being required to suppress explosion as compared with 0.002 per cent of iodine in a similar experiment.¹⁰

A vast number of experiments have been carried out in which reaction in oxygen-hydrogen mixtures is initiated by atoms, by ions, or by molecules in higher quantum states. Tremendous broadening of the ignition region is produced by these additions. The production of active centers by electric discharges passed through the mixture, by means of which explosions can be obtained at room temperature, which is the best-known example of this effect, has been treated in detail in a preceding paper by Bradford and Finch (see page 112). We shall consider here experiments in which atoms are generated by a discharge through one of the gases before mixing. When hydrogen atoms are produced in this way, at a partial pressure of about 0.05 mm, the explosion limits are con-

siderably widened,⁷ the effect increasing somewhat with the concentration of atomic hydrogen. Atomic oxygen gives a far more striking change, however. With it, ignition of a sort is produced even at room temperature. The upper limit, moreover, either completely disappears or at least recedes beyond the experimental range.²² The different nature of the changes in the limits for the two cases suggests that the addition of atomic hydrogen merely starts more of the normal chains, but that atomic oxygen leads to chains of a new and more fecund kind.¹⁷ There are several difficulties in such a view, however, which will be considered later.

Many other experiments deal with ignition or slow reaction due to atoms of hydrogen, oxygen, or chlorine produced photochemically, either directly or by means of photosensitizers such as mercury vapor.^{23,19,21,3} The most important result of such work is the evidence that slow reaction initiated by either atomic hydrogen or atomic oxygen involves chains which are very short at room temperature, but increase rapidly in length as the temperature nears the ignition region, and that the chief primary product is hydrogen peroxide rather than water.

The Reaction Mechanism

The general features of the interpretation of these results are the same as have been discussed in the preceding paper on the mechanism of combustion of hydrocarbons. The greater chemical simplicity of the present reaction, however, makes it reasonable to expect the details of the mechanism to be established more completely and more definitely. As yet, unfortunately, this represents more a hope for the future than an accomplishment of the past.

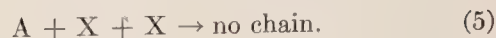
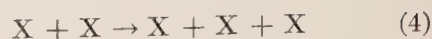
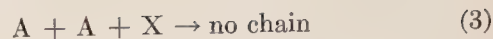
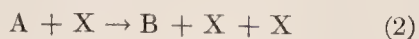
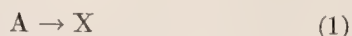
The ignition region is unquestionably due to a chain reaction. The chains ordinarily start on the walls, but a few originate in the gas.^{1,12a} Branching occurs in the gas. The chains may be broken either by a triple collision in the gas, or by diffusion to the wall. Ignition takes place, according to the simple theory, when the rate of branching is greater than the rate of breaking. This mechanism gives upper and lower limits to the ignition region. At the upper limit chain breaking is predominantly due to triple collisions. Hence the limit is nearly independent of factors which influence the rate of chain breaking at the walls, that is, of the vessel diameter and of the material and pretreatment of the reaction vessel. Inert gases break chains at triple collisions and hence reduce the upper limit. The lower limit, on the other hand, is determined predominantly by the rate of chain breaking at the walls. It is therefore sensitive to the nature of the

walls and to the size of the vessel. Inert gases retard diffusion, and thus lower the lower limit. If no chains start, there can be no ignition, but according to the simple theory any finite rate of starting, however small, is sufficient to give ignition if the net branching rate is greater than zero. In the Alyea-Haber experiment with crossed streams, however, ignition will not be observed unless it develops to a sufficient extent before the crossed streams have been too much weakened by diffusion; in the absence of suitable surface the rate at which chains start in the gas alone does not seem to fulfill this condition below 560°C. Likewise in an aluminum vessel, so few chains start that they do not have time to develop sufficiently before the catalytically formed steam has wiped out the ignition region. When a silica surface also is present, chains start more rapidly, and ignition occurs. The results in a silver vessel seem to require a different explanation, which will be discussed later.

The effects of sensitizers and inhibitors can be understood in principle as due to their creation of new possibilities for chain branching and chain breaking. A single substance may participate in both processes and thus function in both roles, as nitrogen dioxide appears to do.

The broadening of the ignition region by artificial creation of chain carriers does not fit easily into the framework of the classical theory. The results with atomic oxygen might be interpreted as representing an entirely new chain, with new limits; the effect of atomic hydrogen, however, is quite obviously a mere broadening of the already existent limits. A possible interpretation is that in addition to the set of branching and breaking reactions involving a single carrier and fixing the normal limits, there are additional branching and breaking reactions involving two carriers in each step, which would, if left to themselves, determine wider limits. For mixtures beyond the normal ignition limits, the first set of reactions alone would determine a steady concentration of chain carriers dependent on the rate of starting chains. If this steady concentration is small enough, it is not appreciably altered by the existence of the second-order reactions. But if the first-order reactions permit the number of chain carriers to increase sufficiently, the second-order set will take command and lead to ignition.

This interpretation may be illustrated by the following very formal example, where normal chain-carrying reactions are omitted, only starting, branching, and breaking steps being shown.



Then

$$dX/dt = k_1A + (k_2A - k_3A'^2)X + (k_4 - k_5A)X^2.$$

The condition for ignition is that $dX/dt > 0$ for all values of X . This condition cannot be fulfilled unless

$$k_4 - k_5A > 0, \quad (I)$$

and also either

$$k_2A - k_3A^2 > 0 \quad (II)$$

or

$$k_1A > (k_2A - k_3A^2)^2/4(k_4 - k_5A). \quad (III)$$

Values of A for which Expression II is not satisfied, but both I and III are, represent broadening of the ignition region. It is evident that the amount of this broadening is greater the greater k_1A is, that is, the faster chains are being started.

In many experiments, the conditions are better described as a high initial value of X than by a large value of k_1A . The condition for ignition in such cases is that $dX/dt > 0$ for all $X > X_0$. If k_1A can be neglected, which is probably a reasonable approximation under these conditions, ignition will occur if

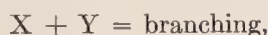
$$X_0 > (k_3A^2 - k_2A)/(k_4 - k_5A). \quad (IV)$$

Here also, as the initial concentration of chains is increased, the normal limits are progressively widened.

It is obvious that any dependable theory of the lower limit and of the high-pressure gas reaction as well must be based on a sound treatment of the rate of breaking chains at the surface. In many cases it has been thought sufficient to take the surface breaking as equivalent to a volume rate of breaking kn/pd^2 , where n is the average concentration of chains, p is a linear function of the various partial pressures, and d is a linear dimension of the vessel. This treatment can in fact be justified by a consideration of the diffusion Eq. (5), subject to three conditions: (a) every chain reaching the wall is destroyed; (b) the net rate of branching is proportional to the number of chains in existence; and (c) branching occurs at only a small fraction of all chain-continuing reactions. When the fraction of chains destroyed by a single collision with the walls is a fraction $\epsilon > 1$, and Conditions (b) and (c) are fulfilled, rather different results are obtained.^{18,27} In the range $1 > \epsilon > 0.01$, the rate of breaking at the wall is scarcely dependent on the

value of ϵ and the preceding simple rate law is nearly obeyed. As ϵ decreases below 0.01, the rate law changes gradually from kn/pd^2 to $3\epsilon\bar{v}n/2d$, where \bar{v} is the mean molecular velocity. In the upper range the rate of breaking is nearly independent of the condition of the surface, and nearly inversely proportional to the diffusion coefficient and to the square of the diameter. In the lower range it is nearly proportional to the chain-breaking efficiency of the surface, nearly independent of the diffusion coefficient, and nearly inversely proportional to the first power of the diameter. When either (b) or (c) is not satisfied, special investigation is required. Such an investigation with regard to c appears farther on in this paper.

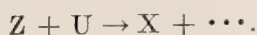
One of the most puzzling features of this reaction has been the relation between the chain in the ignition region and that in the high-pressure gas reaction. Thompson and Hinshelwood²⁵ had originally postulated totally different chains in the two regions. This unsatisfying view was rejected by Grant and Hinshelwood,¹³ who proposed the following formal theory. Normally the upper limit might be described by



They suggested that if the role of M at a triple collision was not to break the original chain but merely to prevent branching, sufficient chains would survive to provide the gas reaction above the upper limit. Kinetic analysis of this theory, however, showed¹⁸ that it predicted totally wrong characteristics both for the gas reaction and for the upper limit, and it seemed necessary to return to the idea of unrelated chains. Very recently, von Elbe and Lewis have found a more plausible interpretation.²⁶ The upper limit is caused by triple collisions



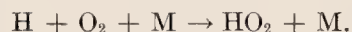
Z is neither a perfectly stable molecule nor a real chain carrier. At the upper limit it is destroyed by diffusion to the walls, but above the limit this diffusion becomes increasingly slow and there is time for Z to regenerate chains by some reaction such as



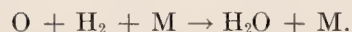
This theory can even account formally for a third isothermal explosion limit, although, as von Elbe and Lewis point out, the actually observed third limit is probably a thermal explosion.

Specific Mechanisms

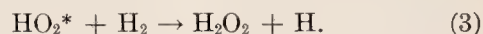
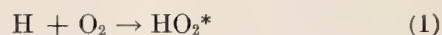
The foregoing analysis has provided only skeleton mechanisms. We shall now consider the problem of replacing noncommittal X's and Y's with specific intermediates. A systematic treatment of this problem, for the normal ignition limits, was attempted by Kassel and Storch,¹⁸ who constructed a catalog of all imaginable reactions involving only a single chain carrier, and investigated the conditions under which the resulting complicated equation for the upper limit would reduce to the correct experimental form. They found two solutions. In one, branching took place at collisions $H + O_2$, breaking by



HO_2 was not a chain carrier. The second, less plausible, solution involved branching at collisions $O + H_2$, and breaking by



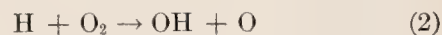
The first solution envisaged the normal chain as (the numbering follows that of Kassel and Storch, with additions as necessary)



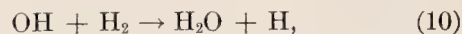
The chains were broken by



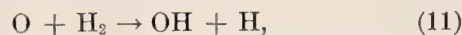
The distinction between HO_2 and HO_2^* was that the latter possessed its heat of formation and was an active chain carrier, while the former did not continue the chain. It was necessary for this distinction to be a sharp one, that is, the rate of reaction of HO_2^* with H_2 had to be large compared to its rate of deactivation to HO_2 by collision with other molecules; if this was not the case, the resulting expression for the upper limit was incorrect. Branching could occur by one or both of



Since all HO_2^* reacted with H_2 , the second of these branching reactions was kinetically equivalent to the first. Branching was completed by



which had to be the only important reaction of OH. If Reaction (2) was a branching reaction it was necessary to have also

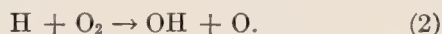


which had to be the only important reaction of O.

The occurrence of



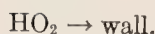
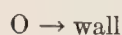
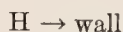
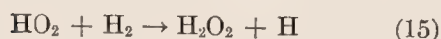
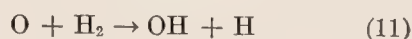
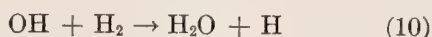
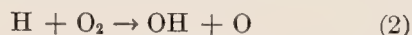
in this mechanism was based on the authors' reluctant acceptance of the Bates and Lavin² view that HO_2 could be formed in a bimolecular association reaction. It is now firmly established by the work of Cook and Bates,⁶ Farkas and Sachsse,⁸ and Bodenstein and Schenk⁴ that this reaction occurs only at triple collisions. It has been pointed out by von Elbe and Lewis²⁶ that the mechanism remains unharmed when Steps (1), (3), and (5) are deleted. The effectively slow chain step is now



All O and OH formed in Reaction (2) react by Eq. (10) and (11), so that the stoichiometric result of Reaction (2) is

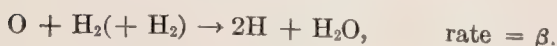
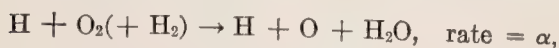


The complete mechanism to account for the ignition region and the high-pressure gas reaction should then be



We shall proceed to a systematic development of the consequences of this mechanism. Since the chain branches at every link, the earlier treatment of the diffusion equation given by Kassel and Storch¹⁸ is not applicable. For an exact treatment it would be necessary to solve four simultaneous diffusion equations. This will not be attempted; instead, various plausible approximations will be investigated separately.

One such approximation which might be applicable at the lower limit is to neglect Reactions (14) and (15), and to assume that Reaction (10) is very rapid. The kinetic equations for the lower limit are then



The diffusion equations for plane parallel plates are

$$\partial \text{H} / \partial t = D_{\text{H}}(\partial^2 \text{H} / \partial r^2) + 2\beta \text{O} = 0$$

$$\partial \text{O} / \partial t = D_{\text{O}}(\partial^2 \text{O} / \partial r^2) + \alpha \text{H} - \beta \text{O} = 0.$$

The most general solution which is permitted by the physical requirements is

$$\begin{aligned} \text{O} = & A \cos(\beta/2D_{\text{O}})^{1/2} R_+ r \\ & + B \cos(\beta/2D_{\text{O}})^{1/2} R_- r, \end{aligned}$$

$$\begin{aligned} \text{H} = & A(\beta/2\alpha)(R_+^2 + 2) \cos(\beta/2D_{\text{O}})^{1/2} R_+ r \\ & + B(\beta/2\alpha)(R_-^2 + 2) \cos(\beta/2D_{\text{O}})^{1/2} R_- r, \end{aligned}$$

where

$$R_{\pm} = [-1 \pm (1 + 8\alpha D_{\text{O}}/\beta D_{\text{H}})^{1/2}]^{1/2}.$$

Equating the net branching rate in the gas to the rate of destruction by the walls gives

$$\begin{aligned} (\epsilon_{\text{O}} \bar{v}_{\text{O}}/4)[& A \cos(\beta/2D_{\text{O}})^{1/2} R_+ r_0 \\ & + A(\beta/2D_{\text{O}})^{1/2} R_+ \lambda \sin(\beta/2D_{\text{O}})^{1/2} R_+ r_0 \\ & + B \cos(\beta/2D_{\text{O}})^{1/2} R_- r_0 \\ & + B(\beta/2D_{\text{O}})^{1/2} R_- \lambda \sin(\beta/2D_{\text{O}})^{1/2} R_- r_0] \\ = & AR_+(\beta D_{\text{O}}/2)^{1/2} \sin(\beta/2D_{\text{O}})^{1/2} R_+ r_0 \\ & + BR_-(\beta D_{\text{O}}/2)^{1/2} \sin(\beta/2D_{\text{O}})^{1/2} R_- r_0 \end{aligned}$$

and

$$\begin{aligned} (\epsilon_{\text{H}} \bar{v}_{\text{H}}/4)[& -A(\beta/2\alpha)R_-^2 \cos(\beta/2D_{\text{O}})^{1/2} R_+ r_0 \\ & - A(\beta/\alpha)(-\alpha/D_{\text{H}})^{1/2} R_- \lambda \sin(\beta/2D_{\text{O}})^{1/2} R_+ r_0 \\ & - B(\beta/2\alpha)R_+^2 \cos(\beta/2D_{\text{O}})^{1/2} R_- r_0 \\ & - B(\beta/\alpha)(-\alpha/D_{\text{H}})^{1/2} R_+ \lambda \sin(\beta/2D_{\text{O}})^{1/2} R_- r_0] \\ = & (A/R_+)(8\beta D_{\text{O}})^{1/2} \sin(\beta/2D_{\text{O}})^{1/2} R_+ r_0 \\ & + (B/R_-)(8\beta D_{\text{O}})^{1/2} \sin(\beta/2D_{\text{O}})^{1/2} R_- r_0. \end{aligned}$$

These two equations determine A/B and r_0 . Since no simple explicit solution for r_0 can be found, it is hard to visualize the results. We may, however, investigate a few extreme assumptions.

Case I.

$$\epsilon_{\text{H}} = \epsilon_{\text{O}} = 1.$$

Here the solution is simply

$$B = 0,$$

$$(\beta/2D_{\text{O}})R_+^2 r_0^2 = \pi^2/4.$$

Since

$$D_{\text{O}}^{-1} = g_{\text{H}}(\text{H}_2) + g_{\text{O}}(\text{O}_2) + g_{\text{X}}(\text{X})$$

and β is proportional to (H_2) , this becomes

$$(\text{H}_2)[g_{\text{H}}(\text{H}_2) + g_{\text{O}}(\text{O}_2) + g_{\text{X}}(\text{X})]R_+^2 r_0^2 = \text{const.}$$

The two possible extreme cases are

$$\alpha D_O \gg \beta D_H \quad R_+^2 = (8\alpha D_O / \beta D_H)^{1/2}$$

and

$$\alpha D_O \gg \beta D_H \quad R_+^2 = 4\alpha D_O / \beta D_H.$$

The corresponding conditions for the lower limit are

$$(H_2)^{1/2}(O_2)^{1/2}[g_H(H_2) + g_O(O_2) + g_X(X)]r_0^2 = \text{const.}$$

and

$$(O_2)[g_H(H_2) + g_O(O_2) + g_X(X)]r_0^2 = \text{const.}$$

The latter of these corresponds in form with the Frost and Alyea expression for the lower limit in potassium chloride on Pyrex.

Case II.

$$\epsilon_H = 0 \quad \epsilon_O = 1.$$

It is easily seen that for this case the chains branch faster than they can be broken, and there can be no lower limit. This same conclusion can be reached from the general equations, but only after considerable algebra.

Case III.

$$\epsilon_H = 1 \quad \epsilon_O = 0.$$

For this case also the lower limit is given by

$$(O_2)[g_H(H_2) + g_O(O_2) + g_X(X)]r_0^2 = \text{const.}$$

A far more thorough investigation should be made, but it seems likely that the lower limit data of Frost and Alyea as well as those of Hinshelwood¹⁵ are reconcilable with this mechanism.

The upper limit is treated by neglecting Reaction (15) and all wall reactions except the destruction of HO_2 , which is supposed to be fast. The limit is then given by

$$k_{14,H}(H_2) + k_{14,O}(O_2) + k_{14,X}(X) = 2k_2.$$

Since there is no reason to expect that the various k_{14} values have appreciable temperature coefficients, comparison with experimental results requires an activation energy of 24 to 26 kg-cal for Reaction (2). This reaction could then take place at only 1 collision in 10^7 at 550°C . Such a value seems rather small in comparison with the probable rate of triple collision.

For the reaction above the upper limit we restore Reaction (15) and take the rate of destruction of HO_2 on the wall as $k_w(HO_2)/X d^2$, a form which is approximately correct when the chains start in the gas and are destroyed at

nearly every collision of HO_2 on the wall.²⁷ The rate of starting chains is represented formally by S . Then

$$\frac{d(H_2O)}{dt} = \frac{2k_2 S [k_{15}(H_2)(X)d^2 + k_w] + k_{14}k_{15}(H_2)(X)^2 d^2}{k_{14}k_w(X) - 2k_2[k_{15}(H_2)(X)d^2 + k_w]}.$$

It is possible to show that this equation reproduces at least all the striking qualitative characteristics of the reaction above the limit.

This mechanism thus seems to account for everything to which it is reasonably applicable, *except for the results in silver vessels*. This problem has been discussed fully by von Elbe and Lewis.²⁶ Undoubtedly chains are broken faster in silver vessels than in glass, quartz, or alumina; this cannot be because walls of the latter substances break chains very inefficiently, since in that case the observed lower limit must be inversely proportional to the first power of the diameter and independent of inert gas. These authors have suggested breaking in the gas phase by silver sputtered from the surface by the exothermic reactions occurring there.

Space does not permit any elaborate discussion of the role of inhibitors and sensitizers. The mechanism of inhibition by halogens has always been rather clear.

The reactions



are rapid in all cases, and serve to remove chain carriers. The reaction



is also rapid, while the corresponding reactions with bromine and iodine are slow; the relatively weak inhibition by chlorine is thus easily understandable.

The more interesting effects due to addition of nitrogen dioxide have received considerable attention. A mechanism for it has recently been found by von Elbe and Lewis²⁸ which is consistent with that given above for the nonsensitized reaction, and which will probably stand or fall with the latter.

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THEORY OF FLAME PROPAGATION*

BERNARD LEWIS

Explosives Division, Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pennsylvania
AND

GUENTHER VON ELBE

Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pennsylvania

The purpose of this paper is to discuss the mechanism of the propagation of flame through a combustible mixture relative to the unburnt gas. This rate of flame propagation is sometimes referred to as the fundamental speed of flame or transformation velocity or burning velocity. The considerations will be confined to burning velocities that are far below the velocity of sound, as distinct from detonations that travel with speeds greater than the velocity of sound. The problem of the burning velocity is obviously very complex, the process of flame propagation being dependent on heat flow, on diffusion of

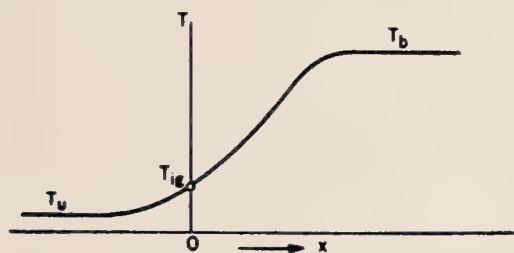


FIGURE 1

many species, particularly active ones such as atoms and radicals, and on kinetics of complex reactions. Therefore at present any theory must necessarily involve hypotheses and approximations.

The study of chemical kinetics is a comparatively recent development. It was natural, therefore, that in the first attempts¹⁰ the problem should have been regarded as one involving primarily the conduction of heat from the burnt to the unburnt gas. To illustrate, let us consider the reaction zone stationary with respect to the coordinate system x - T in Fig. 1. The unburnt gas at the temperature T_u moves in the direction of the arrow against the heat flow along the temperature gradient between the final temperature T_b (after complete combustion) and T_u . When its temperature has risen to the ignition temperature T_{ig} , reaction commences and continues until T_b is established. Taken as

it is, no serious objections could be raised against this picture even today, provided the proper limitation is placed on the interpretation of T_{ig} . It was widely supposed that this temperature was something of the nature of a physical constant of the gas mixture that could be determined in independent experiments. As was perhaps evident in the first section of this symposium on the kinetics of ignition, the ignition temperature is not a physical constant of the gas mixture but is a function of the system as a whole in which ignition occurs and of time (ignition lag). For the case of flame movement it is almost certain that no experiment could be performed that would ensure conditions that simulate those that define T_{ig} . This is quite apart from the consideration that T_{ig} , even according to older views of reaction kinetics, would not be a sharply defined temperature but would comprise a certain, possibly small, temperature range within which the reaction becomes so fast that during the further travel of a gas element from T_{ig} to T_b the percentage of heat evolution is commensurate with the percentage of distance traveled.

Several attempts have been made to derive an expression for the burning velocity from the foregoing picture. While such derivations cannot lead to a quantitative description, owing to uncertainties in the conception of T_{ig} and the general lack of knowledge of the reaction rate, they lead to some qualitative conclusions that are not without interest. For this purpose a crude mathematical development will suffice.

The zero point of the x -axis is placed at the point where the temperature of the gas has risen to T_{ig} . Consider a stream of combustible mixture of unit area cross section. The unburnt gas at this point is receiving per unit time an amount of thermal energy (required for ignition)

$$H_{ig} = S_u \rho_u \bar{c}_p (T_{ig} - T_u), \quad (1)$$

where S_u is the burning velocity, ρ_u the density of the unburnt gas, \bar{c}_p the average specific heat of the mixture at constant pressure, T_{ig} the ignition temperature, and T_u the temperature of the unburnt gas.

Since this heat is transferred by conduction it must be equal to

$$H_{ig} = \mu (dT/dx)_{x=0}, \quad (2)$$

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TABLE I

Lower limits of inflammability of combustibles in air and oxygen under comparable conditions (*Ref. 4*)

Combustible	Lower limit	
	In air	In oxygen
Hydrogen	9.4	9 to 10
Carbon monoxide	16.3	16.7
Methane	6.1	6.4
Ethylene	3.13	3.1
Propylene	2.00	2.10
Acetylene	3.45	3.1
Diethyl ether	1.85	2.10
Divinyl ether	1.70	1.85
Cyclopropane	2.40	2.45

where μ is the coefficient of heat conductivity. If it is assumed as a first approximation that $(dT/dx)_{x=0}$ is proportional to $T_b - T_{ig}$, i.e., the temperature gradient between T_b and T_{ig} is substantially linear, then

$$H_{ig} = \mu(T_b - T_{ig})x_b^{-1}, \tag{3}$$

where x_b represents the thickness of the reaction zone between T_{ig} and T_b and is a function of the reaction rate. It becomes smaller the faster the reaction.

Combining Eqs. (1) and (3), one obtains

$$S_u = \frac{\mu}{\rho_u \bar{c}_p} \frac{T_b - T_{ig}}{T_{ig} - T_u} x_b^{-1}. \tag{4}$$

This is substantially the equation originally proposed by Mallard and Le Chatelier.¹⁰

Equation (4) predicts the existence of limits of inflammability. With sufficiently lean or rich mixtures T_b will decrease, and, although T_{ig} is presumably a complicated function of mixture composition and other factors, it is evident that $T_b - T_{ig}$ must vanish while $T_{ig} - T_u$ remains positive and finite. If in lean mixtures the nitrogen of the air is replaced by oxygen, \bar{c}_p , μ , and T_b will not change very much. Neither will the diffusion characteristics of the mixture and the reaction velocity change very much, so that it is not unreasonable to consider T_{ig} and x_b substantially unchanged. Thus it can be understood that the lower limit of inflammability is little different in air and in oxygen, as was also pointed out by Jost⁵ and as Table I shows.

For the same reason it is understandable that in sufficiently lean mixtures the substitution of oxygen for nitrogen has little effect on the burning velocity. This is shown in Table II.

If T_{ig} is reasonably constant over a range of

mixture composition near the stoichiometric, the ratio $(T_b - T_{ig})/(T_{ig} - T_u)$ goes through a maximum for the maximum T_b ; furthermore, x_b presumably goes through a minimum at the maximum T_b . Therefore one can understand the near coincidence of the maximum burning velocity mixture and the maximum flame temperature mixture, both being slightly on the rich side.

The nature of an inert component of the gas mixture will affect principally \bar{c}_p , μ , and T_b . If nitrogen is replaced by carbon dioxide, whose specific heat is larger and heat conductivity smaller, the burning velocity should decrease. This is found experimentally.⁴ If nitrogen is replaced by argon, whose specific heat is much lower, the burning velocity should increase, which is confirmed experimentally.¹³ Replacing the argon by helium increases the burning velocity still further,^{3,8} which is in qualitative agreement with the larger heat conductivity of helium. [See also Jost⁵ for such comparisons.] The data show, however, that the increase in burning velocity is by no means as large as the increase in the heat conductivity of the mixture. Therefore one would have to postulate a higher T_{ig} or larger x_b or both in helium mixtures. This is not unreasonable from kinetic experience, since T_{ig} would be higher the lower the local concentration of chain carriers, that is, the larger the diffusion coefficient of the mixture. For the same reason the reaction velocity in any layer dx

TABLE II

Burning velocities of combustibles in mixtures of oxygen and nitrogen (*Ref. 4*)

Mixtures	Burning velocity, cm/sec
30% of (97.15% CO + 1.5% H ₂ + 1.35% H ₂ O):	
in (70% N ₂ + 30% O ₂)	31
in (60% N ₂ + 40% O ₂)	34
in (40% N ₂ + 60% O ₂)	37
in (1.5% N ₂ + 98.5% O ₂)	39
30% H ₂ :	
in (60% N ₂ + 40% O ₂)	240
in (50% N ₂ + 50% O ₂)	250
in (30% N ₂ + 70% O ₂)	260
in (1.5% N ₂ + 98.5% O ₂)	300
10% CH ₄	
in (60% N ₂ + 40% O ₂)	60
in (1.5% N ₂ + 98.5% O ₂)	75

would be retarded and the thickness of the flame front increased. Thus one begins to recognize the importance of diffusion phenomena in the flame front.

Equation (4) can be derived in a different way. The differential equation expressing that in any layer dx of the stationary reaction zone the rate of change of temperature is zero, is given by

$$\mu \frac{\partial^2 T}{\partial x^2} - \bar{c}_p \rho_u S_u \frac{\partial T}{\partial x} + \frac{\partial H}{\partial t} = 0. \quad (5)$$

The terms in this equation represent the rate of change of thermal energy due to conduction, mass flow, and chemical reaction, respectively. According to the approximation of Mallard and Le Chatelier, $\partial T/\partial x$ is a constant between 0 and x_b , and since $\partial H/\partial t = 0$ for $x < 0$, Eq. (5) is easily integrated to give Eq. (4).

The Mallard-Le Chatelier equation is sometimes given in another form. The rate of heat liberation for constant $\partial T/\partial x$ between 0 and x_b is, from Eq. (5),

$$\frac{\partial H}{\partial t} = \rho_u S_u \bar{c}_p \frac{(T_b - T_{ig})}{x_b}. \quad (6)$$

If f denotes the reaction rate, defined as the mass of gas that is reacting in the time dt as the gas passes through the layer dx , then

$$\partial H/\partial t = f \bar{c}_p (T_b - T_u). \quad (7)$$

Combining Eqs. (6) and (7) and eliminating x_b in Eq. (4), one obtains

$$S_u^2 = \frac{\mu}{\rho_u^2 \bar{c}_n} \frac{T_b - T_u}{T_{ig} - T_u} f. \quad (8)$$

For the purpose of drawing qualitative conclusions this form has little advantage over the original Mallard and Le Chatelier equation.

Further refinements of the treatment were made by Jouguet,⁶ Nusselt,¹¹ and Daniell.² In these treatments the temperature gradient between T_b and T_{ig} and the reaction rate were considered to vary along the x -axis. It will be noted from Eq. (5) that the assumption of some temperature distribution along the x -axis automatically fixes the rate of heat liberation, and thus, after introduction of the proper boundary conditions, allows a solution of the problem; this was the procedure chosen by Mallard and Le Chatelier. On the other hand, an assumption concerning the rate of heat liberation along the x -axis does not alone determine the temperature distribution. The refinements mentioned consist of introducing some assumption concerning the progress of the reaction along the x -axis. In order to solve the problem, another equation must be

introduced. Since the mass of gas that enters the reaction zone in unit time equals the mass of gas that undergoes chemical reaction within the zone in unit time, this easily found to be

$$\rho_u S_u = \frac{1}{\bar{c}_p (T_b - T_{ig})} \int_{T_{ig}}^{T_b} \frac{\partial H}{\partial t} \frac{dx}{dT} dT. \quad (9)$$

Considering the extreme difficulty of proposing a satisfactory hypothesis concerning the progress of the reaction along the x -axis, it is evident that these investigations could not have led any further than the Mallard-Le Chatelier treatment. Little has been gained by these attempts beyond a more fully developed mathematical formulism. The incorporation of the cooling effect of the walls in Daniell's treatment of the propagation of flame in tubes may be noted, which demonstrates the existence of a lower critical diameter below which propagation is impossible.

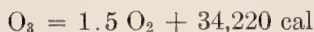
The weakness in all of the above treatments is the concept of ignition temperature as a true physical constant of the gas mixture. In any attempt to develop the theory beyond the stage in which it was left by Mallard and Le Chatelier, it would seem appropriate also to eliminate ignition temperature as an assumed given quantity. In view of the development of reaction kinetics, one must assume that the layer in the unburnt gas in which the reaction becomes fast will be determined not only by a temperature condition but to a large degree by the concentration of active particles or chain carriers. The reaction zone itself may be considered to be abnormally rich in active particles which must diffuse in both directions, toward the burnt and the unburnt gases. The combined effect of diffusion of active particles and heat flow will carry the reaction zone forward into the unburnt gas. It is at once evident that the problem has become considerably more complicated, and it is only by daring approximations that a solution along these lines is at all possible.

One may leave the problem thus unsolved mathematically or attempt a solution with the introduction of approximations. It has, however, become sufficiently clear that diffusion plays an important rôle in the propagation of flame and that this diffusion concerns the migration of chain carriers into the unburnt gas where it renders the latter reactive. A solution has been attempted here, and the results will be given for a particular case.

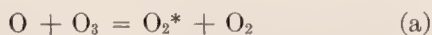
In order to overcome the difficulties inherent in the simultaneous treatment of heat conduction and diffusion, Lewis and von Elbe⁹ proposed the following hypothesis. The sum of thermal and chemical energy per unit mass in any layer dx between the unburnt and burnt gases is sensibly

constant. To consider the consequences of this hypothesis, it will be noted that the chemical energy in the unburnt gas at the temperature T_u is equal to the thermal energy needed to raise the temperature of the burnt gas from T_u to T_b , neglecting the generally inappreciable loss due to radiation. Any layer of gas between the unburnt and burnt gases if allowed to complete its reaction adiabatically would acquire a temperature T_b . The hypothesis may be understood to be based on the following considerations. Since thermal energy flows from the burnt to the unburnt side and chemical energy predominantly in the opposite direction, there is a tendency to equalize deviations from the average total energy content. There will, of course, be an excess of energy in the unburnt gas, formerly denoted by H_{ig} ; this energy "hump" is conceivably much smaller than would correspond to earlier ideas concerning ignition temperature values. The latter may be very low, owing to the presence of active particles which, of course, represent a form of chemical energy imparted to the unburnt gas in excess of its original chemical energy content. However, owing to the property of active particles to promote a reaction efficiently, this excess energy is conceivably very small and the energy hump on the unburnt side is therefore flat.

This hypothesis allows one to confine the analysis to the flow of chemical energy which is transported through the reaction zone by mass flow. Lewis and von Elbe have attempted to develop a theory of the propagation of flames traveling through ozone-oxygen mixtures, the decomposition of ozone being a reaction of comparative simplicity. The over-all reaction



is presumed to proceed by the following steps:

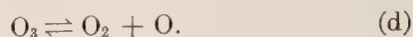


where O_2^* is an energy-rich molecule. One should also take into consideration the reaction



It will be necessary to simplify this mechanism further. It will be assumed that both reactions b and c proceed fast compared to Reaction (a), so that thermodynamic equilibrium between O and O_3 is sensibly established in any layer. This assumption will be in error, particularly on the unburnt side where the concentration of oxygen atoms which have arrived by diffusion will exceed the equilibrium concentration. At higher temperatures, that is, toward the burnt side, it is quite possible that the assumption is not very much in error. Therefore, we shall consider the

mechanism to consist only of Reaction (a) and Reaction (d),



Denoting by N_{O} , N_{O_2} , etc., the number per cubic centimeter of the atoms or molecules indicated by the subscripts, the relation

$$N_{\text{O}}N_{\text{O}_2}/N_{\text{O}_3} = K \quad (10)$$

is thus assumed to hold in any elementary layer dx . K is the equilibrium constant and is a function of temperature. According to published data⁷

$$K = 3.03 \times 10^9 \frac{N_{\text{O}_2(b)}}{P} \frac{T_b}{T} e^{-12,300/T}, \quad (11)$$

where P is the pressure in millimeters of mercury and $N_{\text{O}_2(b)}$ is the number of molecules in 1 cc at the end of the reaction zone, namely where the temperature is T_b .

The hypothesis that the sum of thermal and chemical energy per unit mass is constant in any layer within the reaction zone may be expressed by the equation

$$\begin{aligned} N_{\text{O}_3}E_{\text{O}_3(T)} + N_{\text{O}}E_{\text{O}(T)} \\ = (N_{\text{O}_2} + 1.5 N_{\text{O}_3} + 0.5 N_{\text{O}})C_{pT}T_b(T_b - T), \end{aligned} \quad (12)$$

where $E_{\text{O}_3(T)}$ is the heat of decomposition of 1 mole of ozone at the temperature T ; $E_{\text{O}(T)}$ is the heat of recombination of 1 mole of oxygen atoms at the temperature T and is approximately equal to 59,000 cal; $C_{pT}T_b$ is the mean molar heat capacity of oxygen at constant pressure between the temperatures indicated

Since the burning velocity is small compared to sound velocity, the pressure will be practically constant throughout the reaction zone, and one obtains from the gas law

$$N_{\text{O}_2} + N_{\text{O}_3} + N_{\text{O}} = N_{\text{O}_2(b)}(T_b/T). \quad (13)$$

Since the mixtures whose experimental burning velocities will be compared with the theory contain considerably more oxygen than ozone, no serious error is introduced by the approximation

$$N_{\text{O}_2} \simeq N_{\text{O}_2(b)}(T_b/T). \quad (14)$$

This approximation is particularly allowable at intermediate and higher temperatures because the concentrations of O_3 and O that are required to fulfill Eq. (12) become very small.

From the concentration of O_2 in any layer, the concentrations of O_3 and O and the temperature T in the layer are determined by the foregoing system of equations. The condition for the stationary state is now simply that the rate of change of concentration of O_2 in any layer due to diffusion, mass flow, and chemical reaction

is zero. This leads to

$$D \frac{\partial^2 N_{O_2}}{\partial x^2} - \frac{\partial}{\partial x} (N_{O_2} S_x) + \left(\frac{\partial N_{O_2}}{\partial t} \right)_c = 0 \quad (15)$$

D is the diffusion coefficient. Since the O_2 concentration decreases with increasing temperature [Eq. (14)] and the positive direction of the x -axis is the direction of increasing temperature, the sign of the diffusion term is positive. S_x is the flow velocity through any layer x . Since the percentage of O_2 in the mixture increases in the direction of unburnt to burnt gas, more oxygen molecules are pushed out of the layer dx than are pushed in by mass flow. The second term is therefore negative. The third term is the rate of formation of oxygen molecules by chemical reaction.

S_x can also be interpreted to mean the volume of gas passing unit area per second. Since all volumes S_x contain equal masses, then from the gas law and the increased number of moles due to reaction

$$S_x = S_u \frac{T}{T_u} \frac{1 + 0.5a + m}{1 + m}, \quad (16)$$

where m is the ratio of moles of O_2 to moles of O_3 in the original mixture, and $0 \leq a \leq 1$. However, in conformity with the approximations made in Eq. (14), it is essentially correct, especially for intermediate and higher temperatures, to write

$$S_x = S_u (T/T_u). \quad (17)$$

The diffusion coefficient is given by

$$D = \bar{v}\lambda/3, \quad (18)$$

where \bar{v} is the average molecular velocity and λ the mean free path. For this purpose the gas may be considered to consist entirely of oxygen molecules. Using numerical values¹⁴

$$D = 2.2 \times 10^{-2} (T^{3/2}/P). \quad (19)$$

The rate of formation of O_2 by the chemical reaction is given by the number of successful collisions between O and O per second per cubic centimeter, viz.,

$$(\partial N_{O_2}/\partial t)_c = 2Ze^{-E/RT}, \quad (20)$$

where Z is the collision frequency which is given by

$$Z = 2N_O N_{O_3} \sigma^2_{O, O_3} \left(2\pi RT \frac{M_O + M_{O_3}}{M_O M_{O_3}} \right)^{1/2}, \quad (21)$$

where M_O and M_{O_3} are the molecular weights of O and O_3 . E is the energy of activation, the best available value being about 6000 cal per mole.^{12,15}

It will be recalled that in Eq. (5) the choice of a function for $\partial H/\partial t$ did not suffice to arrive at a solution until Eq. (9) was introduced. Simi-

TABLE III

Comparison of calculated and experimental burning velocities of ozone-oxygen mixtures

P , mm Hg	T_u , °K	T_b , °K	m	S_u	
				Exptl, cm/sec	Calc, cm/sec
624	300	1239	3.054	55	253
2560	427	1343	3.054	158	451
595	302	1922	1.016	160	333
3760	468	2044	1.016	747	664

larly, in the present case, it is necessary to introduce an equation analogous to Eq. (9), which may be written

$$S_u N_{O_3(u)} = \frac{1}{1.5} \int_{T_z}^{T_b} \left(\frac{\partial N_{O_2}}{\partial t} \right)_c dx/dT dT, \quad (22)$$

where $N_{O_3(u)}$ is the concentration of O_3 in the unburnt gas. All equations necessary for the solution of the problem have now been given.

The mathematical development of the equations was carried out by Lewis and von Elbe⁹ and calculations of burning velocities were made for certain mixtures for which experimental values were available. The results are given in Table III.

An agreement exist in the order of magnitude, which, considering the assumptions that had to be introduced, would not seem to be unsatisfactory. This indicates that an analysis of the structure of the reaction zone by the foregoing theory would also lead to agreement in the order of magnitude in the temperature and concentration gradients. Such an analysis is given in Fig. 2. It is seen that the thickness of the flame front is of the order of 10^{-3} to 10^{-4} cm. The distributions of the reaction rate and of the concentration of the chain carriers (oxygen atoms) are of interest. The latter are seen to reach a high local concentration in a zone of a thickness of the order of one hundred mean free paths. One may perhaps generalize this result by stating that high concentrations of chain carriers are needed in order to produce the fast chemical reaction required for the propagation of flames.

Substances that accelerate or retard chemical reaction must also exert a similar influence on the burning velocity. The area under the rate curve in Fig. 2 would be either increased or decreased. Since the activation energy is of less importance at high temperatures, one may suggest that the increase or decrease of the area occurs mainly on the low-temperature side of the rate curve.

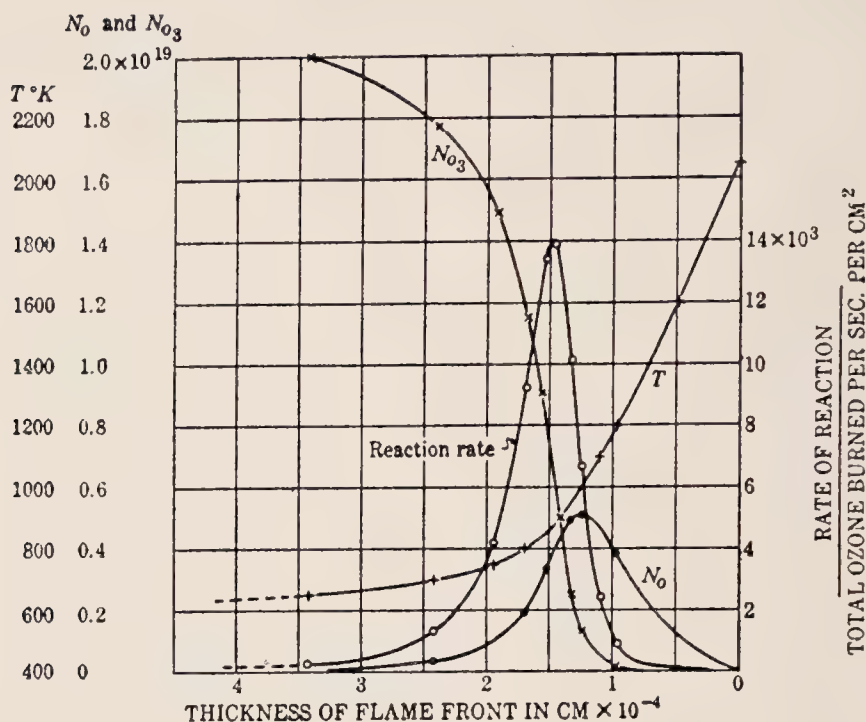


FIG. 2. Structure of reaction zone of ozone flame, showing temperature gradient, distribution of ozone and oxygen atoms, and the reaction rate throughout the zone. 49.6 per cent ozone in oxygen; pressure = 3760 mm Hg; $T_u = 468^\circ\text{K}$; $T_b = 2044^\circ\text{K}$.

Summary

In Mallard and Le Chatelier's treatment of flame propagation the problem is considered simply one of heat flow in which the unburnt gas is raised to its ignition temperature. Although crude, this treatment is able to explain a number of observations: limits of inflammability, effect of diluent gases on the latter and on rate of flame propagation, and near coincidence of maximum flame temperature mixture and maximum speed mixture. Later elaborations of Mallard and Le Chatelier's treatment have not advanced the problem appreciably, due to the indefiniteness of the term "ignition temperature." Certain observations show the importance of diffusion in the treatment of flame propagation. A solution of the problem without the use of ignition temperature has been attempted for the propagation of ozone-oxygen flames, using simplifying assumptions concerning the reaction mechanism and the combined effects of heat flow and diffusion. Agreement in the order of magnitude is found between calculated flame speeds and experimental values. In the flame front there is a steep temperature gradient and also a high local concentration of active species. The width of the flame front is calculated to be of the order of 10^{-3} cm. Some consideration is given to the effect of activators and inhibitors on flame speed.

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PROBLEMS IN FLAME PROPAGATION

H. F. COWARD AND W. PAYMAN

Research Laboratories, Safety in Mines Research Board, Sheffield, England

We suggest that the outstanding problem in flame propagation is to ascertain the mechanism by which flame travels through an inflammable gas mixture, i.e., to correlate the speed of movement of flame with the various chemical and physical factors involved by means of an equation with no empirical constant. It may be expected that when this has been accomplished the solution of most of the other problems in flame propagation will follow immediately or will have been found incidentally. Such a correlation has been made for detonation in gaseous mixtures, on the theory that in this mode of burning the zone of reaction is propagated by a mechanical shock wave maintained by the chemical reaction. In this communication we propose, therefore, to consider only the more usual mode of propagation, in which the pressure of the gas in the flame is not sensibly greater than that of the rest of the gas.

Observed Speeds of Flame

At comparatively low rates the speed of flame relative to an observer is a function of three factors: (a) the movement of the medium in which the flame is travelling, (b) the area of flame relative to the area of cross section of gaseous mixture to which it is exposed, and (c) the speed of flame relative to the gas mixture itself. It has been shown that the observed speed of flame in a moving medium, whose motion may be imposed from without or may be caused by the expansion due to the heat of the flame itself,¹³ is equal to the speed in a still mixture plus the speed of movement of the medium,⁵ and also that the amount of mixture burned is proportional to the area of flame in it.^{11,6}

The fundamental speed of flame (c) is the linear speed of the flame, in a direction at right angles to its surface, through a mixture at rest and at constant temperature and pressure just ahead of the flame. The observed speed of flame travelling in a tube is, therefore,

Fundamental speed

$$\times \frac{\text{area of flame}}{\text{area of cross section of tube}} \\ + \text{speed of movement of medium.}$$

At higher speeds, during what has been termed the predetonation period, compression factors, which attain their maximum effect in detonation, may also exert a pronounced influence.¹⁷

Fundamental Speed of Flame

The conception just defined as the fundamental speed of flame may be what Mallard and Le Chatelier¹³ had in mind when they wrote of "*la vitesse normale*," which was characteristic of "deflagration" (as distinct from detonation) and was, they thought, observable in the propagation of flames, not accelerated by turbulence or by expansion of the burning gases, in tubes wide enough to eliminate the effect of cooling by the walls of the tubes. The term of Mallard and Le Chatelier is as ambiguous in French as in English, we have been informed, in that the word "*normale*" may mean either "ordinary" or "at right angles to its surface." The term "fundamental" is suggested as preferable.⁶

The fundamental speed of flame is the most difficult of all factors to analyze, the others, as has just been shown, being of an obvious mechanical nature. The mode of transfer of energy from the flame front to the neighboring unburnt layers remains to be established, and when physicochemical hypotheses on this process are formulated, they must be tested by measurements of the fundamental speed. What measurements of this are available?

Measurements of the Fundamental Speed of Flame

Le Chatelier's attempt to determine the "*vitesse normale*" from measurements of the speed of flame in tubes was based on the assumption that the flame front was plane and normal to the axis of the tube; the attempt failed because, as was shown later, the flame front is strongly curved.⁴ Three methods have subsequently been used with success. They may be called (a) the Bunsen cone method, (b) the soap-bubble method, and (c) the method based on measurements of the shape of the flame front and its speed of translation during the uniform movement of flame in a tube.

From the dimensions of the inner cone of a Bunsen flame, burning a known mixture at a known rate, can be calculated the component of the linear speed at which the mixture meets the stationary flame, normal to its surface.¹¹ This is reasonably assumed to be equal to the speed of flame in a stationary mixture, but experimental difficulties make some of the results unreliable; for example, flame speeds have been deduced by this method for mixtures containing from 14 to 17 per cent of methane, although these mixtures

do not propagate flame, and mixtures containing less than about 7.3 per cent of methane do not burn on the Bunsen burner, although the lower limit of inflammability of methane is about 5 per cent. These errors are due to the entrainment of air at the orifice of the burner. The measurements of speeds of the more explosive mixtures, containing from 8 to 12 per cent of methane, may be made fairly reliable by careful attention to experimental conditions.⁶

The soap-bubble method, first used by Stevens,¹⁹ depends on measurement of the speed of a spherical flame front travelling in a medium which is put in motion by the flame. From this measurement is deduced the speed in a stationary mixture, on the assumption that the observed speed is equal to the fundamental speed plus the speed of movement of the medium due to thermal expansion. This method is applicable to mixtures which burn at a sufficient rate to make negligible the effects of convection. Its results agree with those of the Bunsen flame method, so far as experiments have been made with the same mixtures.²⁰

The third method is more laborious than the others, and requires more special apparatus. Its results are claimed to be more accurate for the only mixtures to which it has been applied, namely, those of methane and air.⁶

It seems clear that all three methods of measurement lead to the same constant, the fundamental speed of flame, and that one or another method is preferable, according to the nature of the flame. The first is simplest, but reliable only with mixtures of composition near to that of the mixture for complete combustion; the second is successful only with fast burning mixtures; the third is the only accurate method for slow burning mixtures.

Theoretical Analysis of Fundamental Speeds

Mallard and Le Chatelier regarded the "*vitesse normale*" (fundamental speed) as governed by the transfer of heat by conduction from the flame to the nearest unburnt layer of gas, and deduced the formula

$$v = \text{const.} \cdot \frac{k}{c} \cdot \frac{T_f - T_i}{T_i - T_0},$$

in which

k = thermal conductivity,
 c = mean specific heat,
 T_f = temperature of the flame,
 T_i = ignition temperature, and
 T_0 = temperature of the unburnt mixture at some distance from the flame.

Crussard⁸ gave a modified formula, introducing the rate of chemical reaction as a factor:

$$v = \left(kF \frac{v_0}{c} \cdot \frac{T_0}{T_i} \cdot \frac{T_f - T_i}{T_i - T_0} \right)^{\frac{1}{2}},$$

in which F = rate of reaction and v_0 = initial specific volume.

Nusselt¹⁵ gave a somewhat similar formula, but the factor for reaction rate was represented by the concentrations of the reactants. For mixtures of hydrogen and air his equation was

$$v = \text{const.} \cdot \left(k \cdot \frac{p_0 T_0^2}{c} \cdot \frac{T_f - T_i}{T_i - T_0} \cdot [\text{H}_2][\text{O}_2] \right)^{\frac{1}{2}},$$

in which p_0 = pressure and $[\text{H}_2]$, $[\text{O}_2]$ are the concentrations of hydrogen and oxygen.

Daniell⁹ gave the formula

$$v = \left(kF \cdot \frac{v_0}{c} \cdot \frac{T_0}{T_m} \cdot \frac{T_f - T_0}{T_i - T_0} \right)^{\frac{1}{2}},$$

in which T_m is a (harmonic) mean temperature which is probably nearer to T_f than to T_i .

All the foregoing formulas are based on the theory that flame is propagated by conduction of heat (except in the detonation wave) and all contain the independent variable k , the thermal conductivity of the mixture, either as k or $k^{1/2}$. Their validity can readily be tested, for it is easy to prepare series of mixtures which differ greatly in thermal conductivity and very little in any other property which affects the speed of flame. Such mixtures are those of an inflammable mixture with two or more of the inert gases, severally, in the same ratio. The speeds of uniform movement of flame in a series of mixtures of methane and atmospheres approximately $\text{O}_2 + 4\text{A}$ and $\text{O}_2 + 4\text{He}$ were measured some time ago; in mixtures of equal percentages of methane, the speeds with the helium atmospheres were somewhat higher than with the argon atmospheres, but not nearly in proportion to the thermal conductivities of the mixtures.⁷ Some hitherto unpublished observations of a similar character, in which the inflammable gas is hydrogen, are shown in Fig. 1.¹² Moreover, the various mixtures of hydrogen and oxygen propagate flame at speeds which are nearly equal for each pair of mixtures $2\text{H}_2 + \text{O}_2 + n(\text{H}_2 \text{ or } \text{O}_2)$, in spite of the great difference in thermal conductivity according as the one gas or the other is in excess (Fig. 2, drawn from results in Ref. 3).

The comparative measurements just quoted were made on the uniform movement of flame. This is an imperfect basis for comparison unless the areas of the flames are equal, because if, for

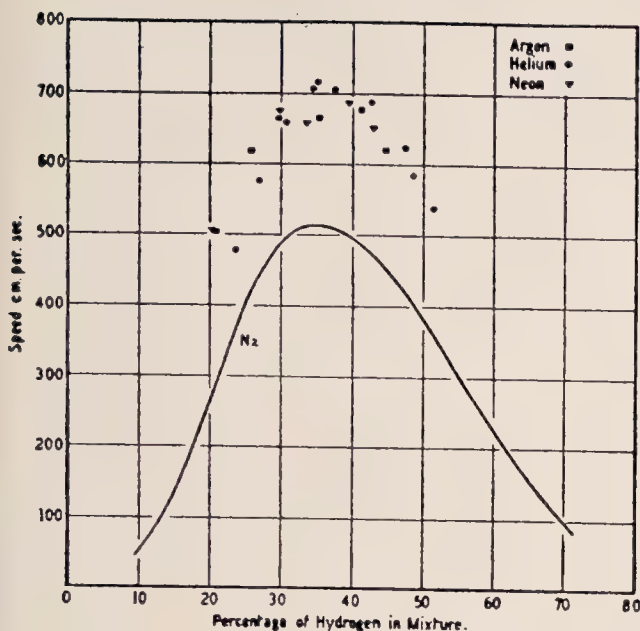


FIG. 1. Speed of uniform movement of flame in mixtures of hydrogen with air (curve N_2) or air in which the nitrogen was replaced by an equal volume of argon or neon or helium. Observations in a tube having a diameter of 2.5 cm.

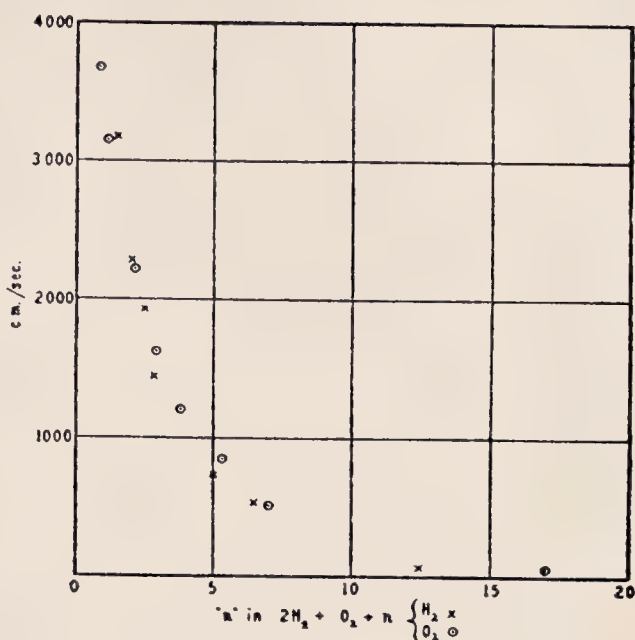


FIG. 2. Speed of uniform movement of flame in mixtures of hydrogen and oxygen. Observations in a tube having a diameter of 2.5 cm.

example, the area of one were n times the area of the other and the speeds of uniform movement were equal, the fundamental speed of the first would be but $1/n$ of that of the other. A series of comparative experiments in which the fundamental speeds of flame were measured has therefore been made,¹² the results of which are shown in Table I.

Although the thermal conductivities of these mixtures at flame temperatures have not been measured, it must surely be that their ratio, or even the square root of their ratio, is much higher than the ratio of the fundamental speeds of flame. Hence the speed of propagation of flame is not correctly expressed by any of the formulas quoted.

The conclusion just reached does not mean that the propagation of flame is not governed by conduction of heat from the burning to the neighboring unburnt layer, for the slow factor in the succession of events may be the chemical reaction itself, and the speed of flame may measure mainly the speed of chemical reaction. Without making any attempt at finality we may now refer briefly to some of the outstanding experimental observations that must guide future theoretical developments.

1. The calorific value of the mixture mainly determines the relative speed of flame in a series of mixtures, in various proportions, of the same constituents. Figure 2 shows this; dilution of the mixture $2H_2 + O_2$ with equal quantities of

TABLE I

Speed of flame in a tube, 2.5 cm in diameter, in mixtures of 10 per cent of methane with 90 per cent of an atmosphere containing argon or helium

Composition of atmosphere, %	Shape of flame front	Speed of uniform movement cm/sec	Area of flame front, cm^2	Fundamental speed of flame cm/sec
Oxygen; 20.9/Helium; 79.1	Symmetrical	206	12.3	82
Oxygen, 20.9/Argon, 79.1	Symmetrical	138	11.4	59

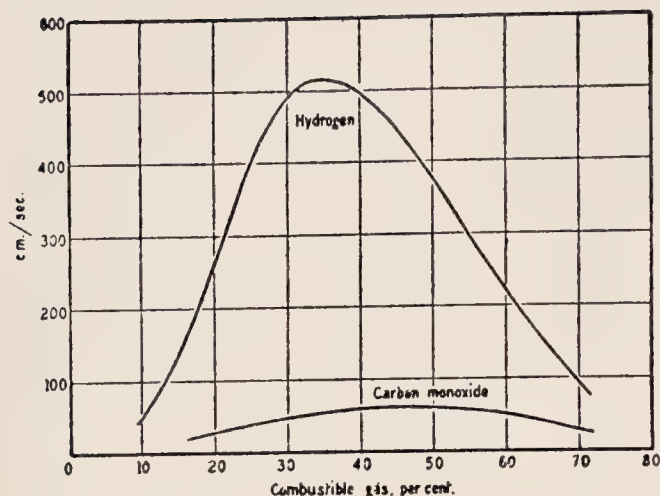


FIG. 3. Speed of uniform movement of flame in mixtures of hydrogen and air, and of carbon monoxide and air. Observations in a tube having a diameter of 2.5 cm.

hydrogen or oxygen caused the same reduction in the speed of "uniform movement" of flame.

The speeds of flame in a series of mixtures of various combustible gases, individually, and air reach a maximum at a composition somewhat on the rich side of the mixture of maximum calorific value. The displacement has been interpreted as an effect of mass action.¹⁶

2. The speeds of flame in various mixtures of equal calorific value may be greatly different; for example, the speeds of uniform movement of flame in mixtures of hydrogen and air on the one hand and carbon monoxide and air on the other, which are shown in Fig. 3. The differences are too great to be due to differences in thermal conductivity, and must be explained by differences in the rates of reaction or in the production of active radicals, or both.

3. Ignition temperatures, corresponding with the very short lags (in time) available in the propagation of flame, have not been determined except perhaps for mixtures of methane and air. It is, therefore, not yet possible to correlate ignition temperatures with the speeds of flame, but in any case an ignition temperature is a function of simpler properties, and so any connection discovered between ignition temperature and flame speed would only be one step towards a final solution of the problem.

4. The propagation of flame is obviously a continuous succession of ignitions of unburnt gas next to the flame front. It might therefore be expected that the most easily ignited mixtures would be those which would propagate flame

most rapidly. This is not so, as the following table will show.

Mixture in which the speed of flame is a maximum	10% methane
Most readily ignitable mixture:	
by heated silica surface	5-6% (Ref. 14)
by adiabatic compression	7-7.5% (Ref. 10)
by impulsive electric spark	8.2-8.3% (Ref. 21)
by the detonation of a solid explosive	8.7-9.3% (Ref. 18)

5. The relative rates of isothermal reaction of a series of mixtures at temperatures below those of ignition are not parallel to the speeds of flame in the same mixtures. Thus at 250°-400°C the most reactive mixtures of each of the simple paraffin hydrocarbons with oxygen are those containing hydrocarbon and oxygen in the molecular proportion 2:1.² Far from these mixtures giving the maximum speed of flame, none of them, at room temperature, can propagate flame.

6. There is evidence that, with hydrocarbons, the course of the chemical reactions is the same in flames as at lower temperatures,^{2,1} but there exist various rival theories of these and other oxidations.

7. Of much significance is the smallness of the effect of large differences in thermal conductivity on the speed of certain flames, other conditions being the same. There must be a less steep temperature gradient in front of the flame in the mixtures of higher thermal conductivity, and preflame reaction must start correspondingly sooner. But the layer of gas just in front of the flame does not ignite any sooner. What is it waiting for? The indication is that the "bursting into flame" is a consequence of the arrival not so much of sufficient heat as of a sufficient concentration of active particles which, provided that they do not lose their activity to or share it with the inert gas, would diffuse at equal rates from the flame front of such mixtures as we are comparing (combustible + oxygen + argon or helium), whereas the diffusion rate of the heat would be different. Hence the active particles owe their efficiency, as propagators of flame, to their chemical nature rather than to their kinetic energy. The conclusion is, therefore, that they belong to some species of radical or atom.

If, however, such an interpretation is to be given to the equality of flame speeds for each pair of mixtures with equal values of n in the

series $2\text{H}_2 + \text{O}_2 + n\text{H}_2$ and $2\text{H}_2 + \text{O}_2 + n\text{O}_2$ (Fig. 2), then the concentration of active particles must be the same in each pair, whether the hydrogen or the oxygen be in excess. More direct evidence that this is so is to be sought.

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THE MEASUREMENT OF FLAME SPEEDS*

ERNEST F. FIOCK AND CHARLES F. MARVIN, JR.

National Bureau of Standards, U.S. Department of Commerce, Washington, D.C.

Introduction

When an explosive mixture of gases is ignited by a spark from within, flame spreads in all directions from the point of ignition. The observed spatial velocity of the flame front in any direction is always the resultant of two component velocities: (1) the speed of propagation relative to the unburned gases; and (2) the speed at which the flame front is transported bodily in a direction normal to its surface by mass movement of the gases comprising it. The first component, or the speed at which the reaction zone advances into and transforms the unburned charge, is a characteristic property of the explosive mixture. This property, which for brevity will be termed the "transformation velocity," has considerable practical and theoretical importance. The second component or "gas velocity" and the resultant speed in space are of minor fundamental interest, since they vary with the size and shape of the explosion vessel and are influenced by general movements initially present in the gaseous charge or established during combustion.

Unfortunately, very few of the many available records of the spatial movement of flame in bombs, tubes, and engines can be analyzed to yield accurate values of transformation velocity. Reliable experimental data showing the separate effects of the various operating factors upon this fundamental flame speed are extremely scarce. Moreover, the micromechanism of flame propagation is still so obscure that there is no adequate basis for calculating transformation velocities from theoretical considerations.

There is need for a clear general picture on a molecular scale of the structure of flame and its mode of propagation which will permit visualization of the effects upon flame speeds of such basic factors as the pressure, temperature, composition and turbulence of the explosive mixture. Accurate experimental values of transformation velocity would be of great assistance in the evolution of a satisfactory theory of flame propagation and are essential to the verification of any such theory.

In the engine, the rate of rise in pressure is largely determined by the transformation velocity of the explosive mixture used. Complete information regarding the effects of composition, temperature, pressure, and turbulence

upon this velocity would be of immediate practical value in predicting and controlling rates of pressure rise. Such data, if extended to sufficiently high temperatures and pressures, should also indicate the conditions for incipient fuel knock. Under these conditions high transformation velocities are to be expected, and autoignition of the unburned charge is probably imminent.

For the reasons which have been enumerated, a primary requisite of a satisfactory method for measuring flame speeds is that it must yield reliable values of transformation velocity. Capacity to function properly over a wide range of operating conditions is a decided advantage. The possibility of obtaining simultaneous information on expansion ratio, heat capacity, equilibrium state, or other factors which influence the amount and rate of the rise in pressure should not be overlooked.

Transformation velocities have been measured for stationary flames and flames moving in tubes and bombs of various shapes. The problems of the stationary flame are discussed by another author.⁶ It is believed that those methods involving spherical flames are susceptible of the most rigorous analysis.

In the present report, both constant-pressure and constant-volume methods involving spherical flames in the absence of detonation are discussed. Applications of these methods are presented and typical results are given to illustrate some of their salient features. The material of this report has been accumulated during the course of investigations sponsored by the National Advisory Committee for Aeronautics.

Constant-Pressure Explosions

One of the simplest methods yet devised for determining transformation velocity is the soap-bubble or constant-pressure method developed by Stevens. This method has been described⁷ and early results obtained by its use have been fully reported before the American Chemical Society,⁷⁻⁹ and elsewhere.^{11,12} A further investigation of the method by Fiock and Roeder² led to a number of refinements in the apparatus and procedure which improved considerably the accuracy of the results obtained and indicated more fully the possibilities and limitations of the method.

Experimental Method. In the improved procedure, a soap bubble, shown in Fig. 1, is blown by introducing a carefully prepared explosive

* Publication approved by the Director of the National Bureau of Standards of the U.S. Department of Commerce.

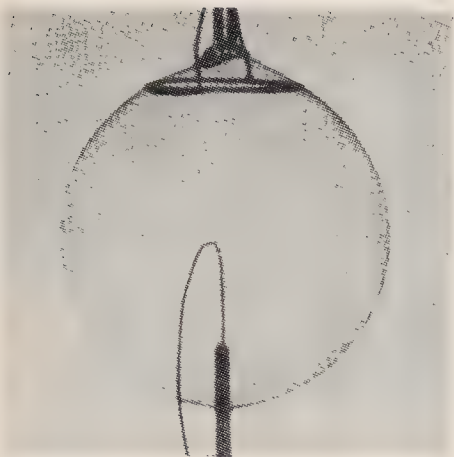


FIG. 1. Soap bubble containing explosive mixture, ready to be fired.

mixture through the glass tube seen at the top of the photograph. The ring of gold wire just below the mouth of the tube helps to support the bubble, which is blown until its horizontal diameter becomes 9 cm, as shown by its projected shadow on an enlarged scale. The electrodes, projecting upward from the bottom, form a spark gap at the center of the full-sized bubble, which may be blown without difficulty with the gap in position.

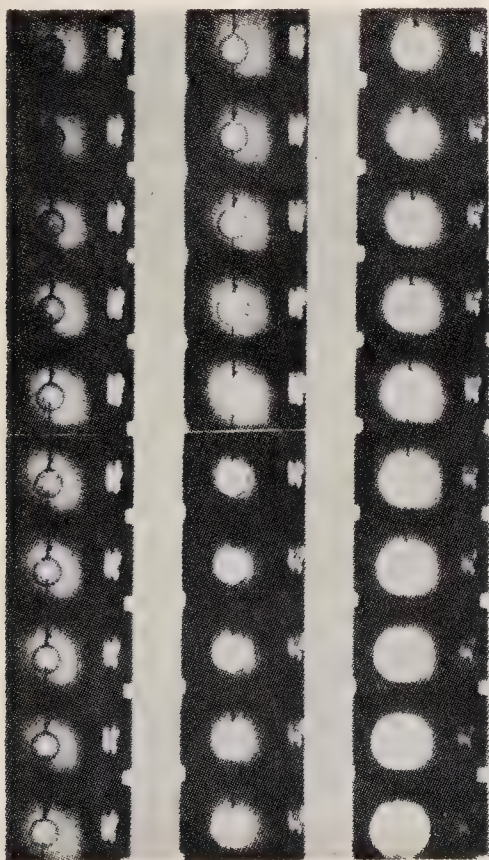


FIG. 2. High-speed motion-picture record of an explosion in a soap bubble (1610 frames per second)

High-speed motion pictures, reproduced in Fig. 2, show that when the spark occurs, a sphere of flame forms at the spark gap and grows steadily in size until all of the explosive mixture is inflamed. During its growth, the flame maintains a spherical shape except for slight local distortions at the supporting ring and the electrodes. The soap film at first distends, then bursts when the flame reaches the gold ring, and finally collapses toward the electrodes without offering appreciable resistance to the progress of the

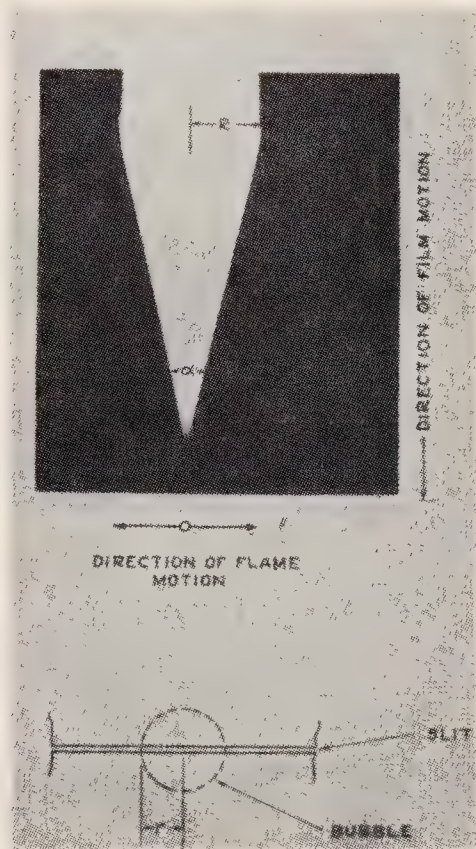


FIG. 3. Method of recording an explosion in a bubble on a rotating film

flame. The explosion thus runs its course at constant pressure. There is no measurable convective rise of the sphere of flame during the period of spread except for very slow-burning mixtures. However, the hot gases subsequently rise out of the picture before they cease to glow.

For analytical purposes, the explosion in the bubble is photographed through a narrow slit which leaves only the horizontal diameter visible. The film is carried on a drum rotating at a known constant speed on an axis parallel to the slit. As the diameter of the sphere of flame increases, its lengthening image moves along the film and produces a V-shaped trace which is a time-displacement record of the travel of the flame front. A typical record is shown in Fig. 3.

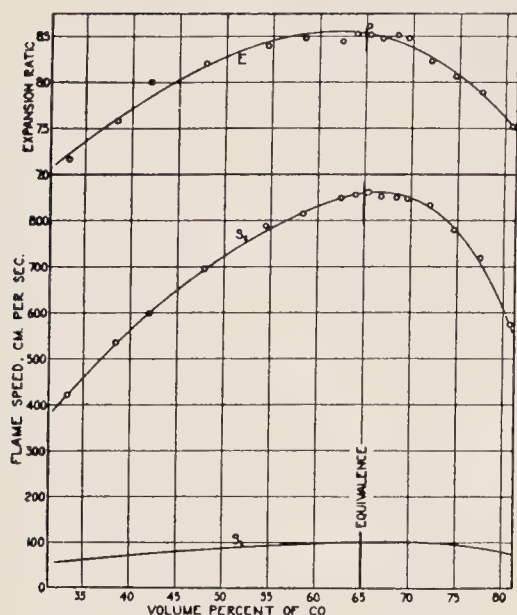


FIG. 4. Effect of fuel-oxygen ratio on combustion characteristics of mixtures of carbon monoxide and oxygen. ($\text{H}_2\text{O} = 2.69$ per cent.)

For most mixtures the sides of the V are practically straight, showing that the flame front travels at constant speed. This speed in space (S_s) can be calculated from the angle (α) of the V, the known speed (F) of the film, and the magnification factor (m) for the camera, through the relation

$$S_s = mF \tan \frac{1}{2}\alpha. \quad (1)$$

Measurements on the film also show that the final diameter of the sphere of hot gases is much greater than the diameter of the original bubble. The ratio of the volume of the burned products to that of the unburned charge is the expansion ratio E for the mixture when burned at constant pressure. If r is the radius of the bubble before firing and R is the maximum radius of the sphere of hot gases as measured on the film, then

$$E = (mR)^3/r^3. \quad (2)$$

The flame not only advances into and transforms the explosive mixture but simultaneously it is carried bodily outward by the expansion of the gases within it. Stevens⁷ showed that the transformation velocity S_t may be computed from the speed in space and expansion ratio through the relation

$$S_t = S_s/E. \quad (3)$$

Values of E may also be used to calculate the temperature of the hot gases at the instant the flame has completed its travel, if sufficient equilibrium data are available from the other sources.²

It was known, prior to the application of the bubble method, that water vapor had a large effect upon the speed of flame in space in mixtures of carbon monoxide and oxygen. For this reason it was necessary to control the quantity of water vapor in the explosive mixtures during the formation and life of the bubbles. It was found by Fiock and Roeder that the transfer of water vapor to or from the atmosphere surrounding the bubble was quite rapid, and that the partial pressure of water vapor had to be made identical in the mixture, the soap solution, and the surrounding air. This was accomplished by blowing the bubbles at the center of a large chamber at a controlled temperature and humidity corresponding to the vapor pressure of the soap solution.

Effect of Fuel-Oxygen Ratio. Since the experiments of Stevens were made without adequate control of the moisture content of the air in which the bubbles were blown, some of his measurements were repeated with more accurate control of conditions. Figure 4 shows the effect of mixture ratio upon flame speeds and expansion ratio for various mixtures of carbon monoxide and oxygen, each initially at 25°C and containing 2.69 per cent of water vapor by volume. The plotted values of E and S_s were calculated directly from measurements on the photographic records. Values of S_t were obtained from the smooth curves for S_s and E .

As a result of a large number of experiments on the system carbon monoxide-oxygen it has been concluded that both S_s and S_t have maximum values slightly on the rich (in carbon monoxide) side of chemical equivalence. Values of E , how-

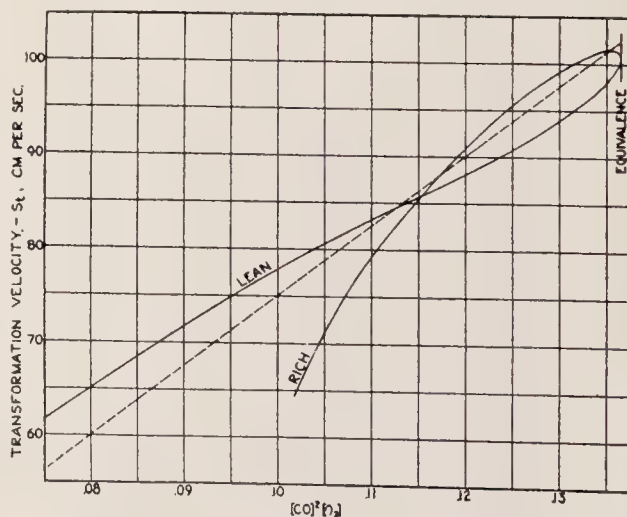


FIG. 5. Relation between transformation velocity (S_t) and the mass action product for mixtures of carbon monoxide and oxygen. ($\text{H}_2\text{O} = 2.69$ per cent.)

ever, change so little on either side of equivalence that it is impossible to locate the maximum from the data available.

All experience indicates that the mechanics of the explosion in a soap film and the method of analyzing the results were correctly postulated by Stevens. However, he concluded that the speed of flame relative to the unburned gas was directly proportional to the mass action product of the concentrations of the active constituents in the original mixture. Applied specifically to the explosive oxidation of carbon monoxide, this statement means that the relation between S_t and the initial concentrations of carbon monoxide and oxygen is expressed by the equation

$$S_t = k[\text{CO}]^2[\text{O}_2], \quad (4)$$

in which k is a constant for each value of water vapor content and the bracketed symbols indicate concentrations of the reactants. The more precise data fail to confirm this relation. Instead of being directly proportional to the mass action product, the transformation velocity varies with it in the complex manner shown in Fig. 5. The

equation, regardless of the value of k , gives a maximum value of S_t at exact equivalence, while the observed maximum values of both S_s and S_t are definitely on the rich side of equivalence. It therefore seems necessary to abandon Stevens' concept of the proportionality of S_t to the initial composition and to resume the search for a relation which is in better accord with the observed facts.

Mixture ratio affects not only flame speed but also the intensity of the light emitted by the explosion. The density of the photographic records decreases on either side of equivalence, as shown in Fig. 6. On the lean side, in the range near equivalence, the afterglow seems to emit more actinic light than the flame front. On the rich side the afterglow soon becomes very faint, then disappears entirely. At both extremes the flame front appears on the records as a line of much greater density than the image of the hot gases which are surrounded by the reaction zone. For very rich mixtures a somewhat irregular flame appears after the excess of fuel has mixed with the oxygen of the surrounding air. In such

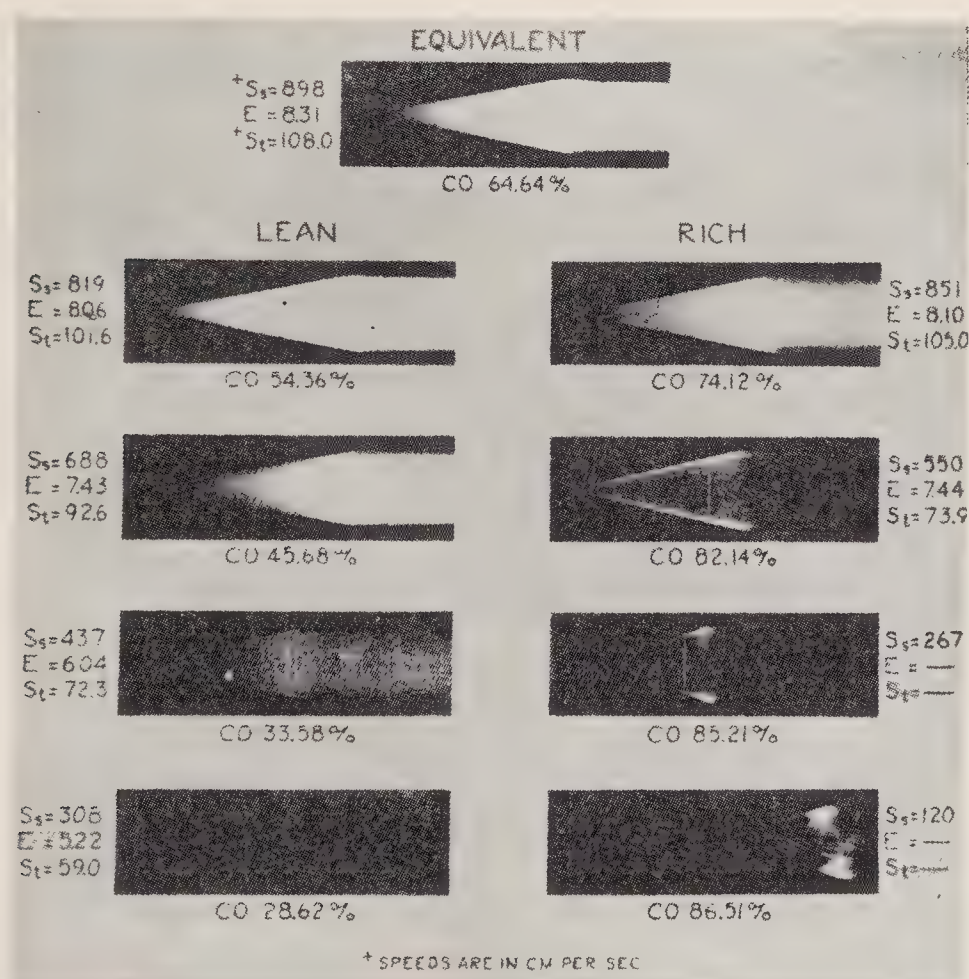


FIG. 6. Photographic records of explosions in bubbles for various mixtures of carbon monoxide and oxygen. ($\text{H}_2\text{O} = 3.31$ per cent.)

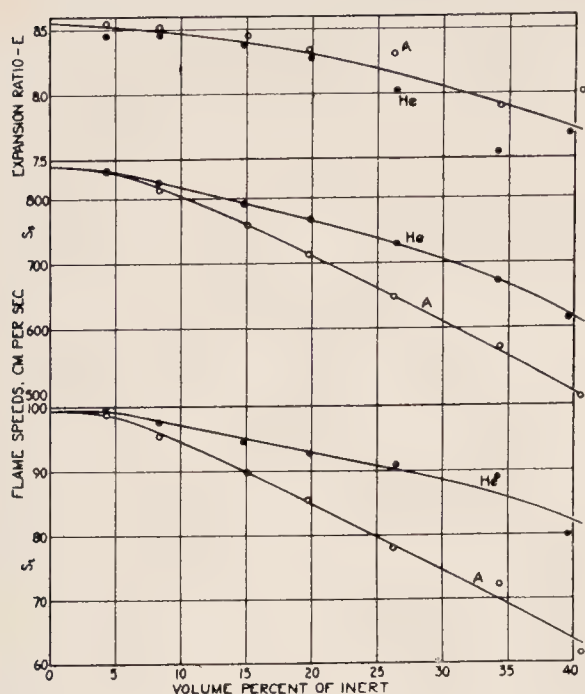


FIG. 7. Effects of argon and helium on combustion characteristics of mixtures of carbon monoxide and oxygen. ($\text{CO}/\text{O}_2 = 1.811$; $\text{H}_2\text{O} = 2.69$ per cent.)

cases the measurement of final volume (and hence also of E and S_t) is impossible.

Effect of Inert Gases. Figure 7 shows the effect on flame speed and expansion ratio of replacing various portions of the active gases carbon monoxide and oxygen with helium or argon. The ratio of carbon monoxide to oxygen had the constant value of 1.811 and the water vapor content was 2.69 per cent throughout. Since it is necessary in the bubble method to hold the moisture content of the mixture constant, the ratio of water vapor to active gas increased as more inert gas was added. From other experiments it is known that such an increase in the proportion of water vapor causes a decrease in E and an increase in S_s and S_t . Thus the decrease in E would have been less and the decrease in S_s and S_t would have been more than that shown by the curves if the ratio of the concentration of carbon monoxide and water vapor could have been kept constant. Similar results have been obtained at various other ratios of carbon monoxide to oxygen³.

The decrease in E with increasing concentration of inert gas is due to the fact that less active mixture and therefore less heat is available to raise the temperature of the same volume of gas. However, the specific heats of both argon and helium are much lower than that of the carbon dioxide which they replace in the final combustion products. Also the lower final temperature

permits a greater conversion of carbon monoxide and oxygen to carbon dioxide and reduces the heat lost by radiation. Because of these effects E decreases more slowly than does the concentration of the active mixture. Interpreted in terms of engine performance, the addition of inert gas would tend to decrease the maximum power available but should increase the efficiency of fuel utilization.

Regardless of the mechanism by which flame propagates, the replacement of active mixture by inert gas may be thought of as the introduction of a resistance, in the form of intermediate collisions, to the transfer of energy in some form from the flame to the unburned gas. The magnitude of the resistance depends upon characteristics of the inert gas which have not yet been definitely identified. Such a resistance is doubtless responsible for the observed decrease in transformation velocity with increasing concentration of inert gas.

Direct comparisons of the effects of like volumes of argon and helium are possible from data at hand. These data show that both argon and helium have practically the same effect upon expansion ratio, but very different effects upon flame speed. For all values of the ratio CO/O_2 from 0.5 to 3.8, a given volume of helium produces a smaller decrease in flame speed than a like volume of argon. The differences in both

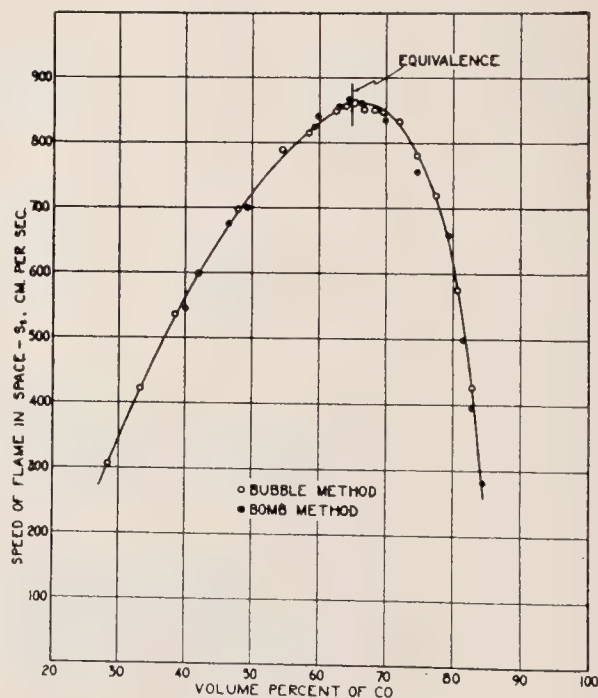


FIG. 8. Speed of flame in space for various mixtures of carbon monoxide and oxygen as determined by the bomb and bubble methods. ($\text{H}_2\text{O} = 2.69$ per cent.)

S_s and S_t produced by like volumes of argon and helium are independent of the fuel-oxygen ratio and approximately proportional to the concentration of inert gas.

Constant-Volume Explosions

Measurements of the Speed of Flame in Space. When an explosion in a closed bomb with transparent walls is photographed, the initial portion of the flame record is identical with that obtained by the bubble method, although the movement of the flame is subsequently modified by the restraining effect of the bomb walls. Figure 8 compares flame speeds in space as determined by the bubble method with corresponding speeds for the same mixtures fired in a bomb made from a glass cylinder 6 in. in diameter and 6 in. long, with metal disks and rubber gaskets sealing the ends. The two sets of data agree within the experimental error.

Substitution of a constant-volume bomb for the soap film makes it possible to vary the water vapor content and the pressure of the mixture independently. Figure 9 shows the effect upon S_s of changing the moisture content in equivalent mixtures of carbon monoxide and oxygen at a number of initial pressures. The explosions at atmospheric pressure were made in the cylindrical bomb just mentioned. The data at lower pressures were obtained in a 5-liter spherical glass flask. Both bombs were provided with central ignition.

From mixtures too dry to ignite or photograph properly to those which were saturated with water vapor at room temperature and the pressure of the experiment, an increase in moisture

content always produced an increase in flame speed. Successive equal increments of moisture have diminishing effects upon flame speed, and there is doubtless some concentration beyond which further addition of water vapor will produce a decrease in flame speed. If it had been practicable to maintain the explosion vessel at an elevated temperature, it is believed that this concentration might have been reached at each of the dry-gas pressures studied. Figure 9 shows also that equal increments of moisture cause more increase in flame speed at the higher pressures. It is quite evident that water-vapor content must be carefully controlled and specified if determinations of flame speed in mixtures of carbon monoxide and oxygen are to be significant.

In normal photographic records of comparatively fast-burning mixtures of carbon monoxide and oxygen, fired in either a soap bubble or bomb, the flame appears to attain its maximum velocity in space at the instant of the spark. If, however, the film is moved at an abnormally high speed, the records show that there is a very short interval, just after ignition, in which the flame has a positive acceleration, as evidenced by the curvature of the traces. The diagram on the right in Fig. 10 shows this early period of flame travel on a magnified scale.

The straight portion of the flame trace SF may be extended until it intersects at point A the axis SD , drawn through the spark S . The time interval SA is the increase in the duration of the explosion caused by the initial slow movement of the flame and will be termed briefly the "delay."

The curve of Fig. 10 shows that the delay increases greatly as the concentration of water

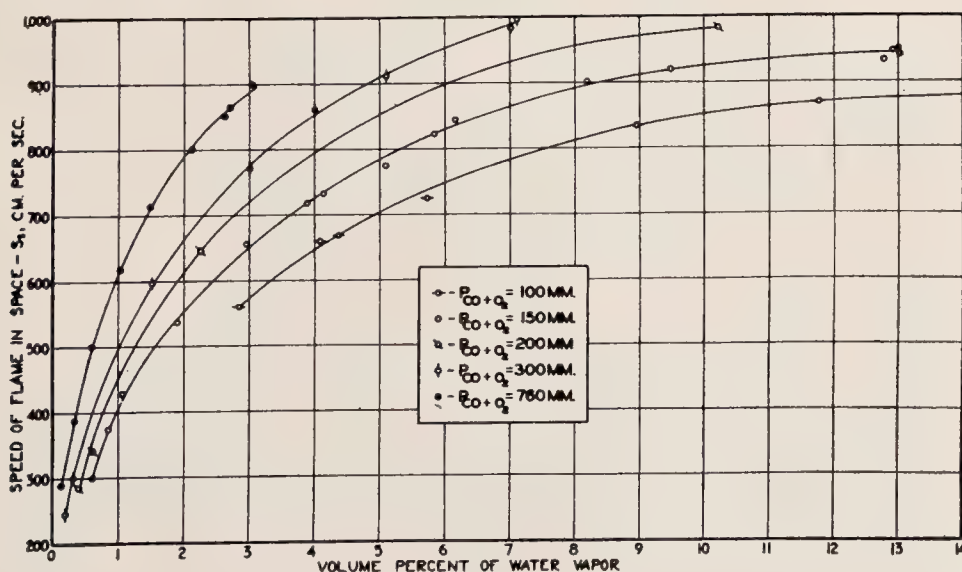


FIG. 9. Effects of water-vapor content and initial pressure on speeds of flame in space for equivalent mixtures of carbon monoxide and oxygen.

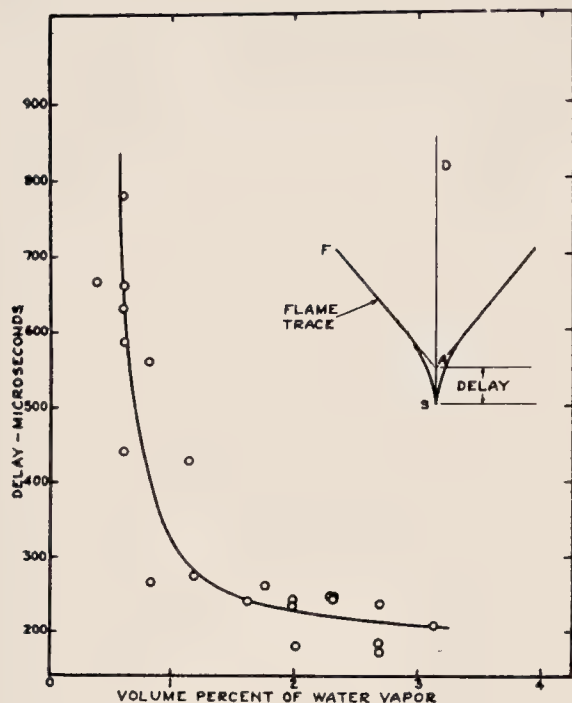


FIG. 10. Effect of moisture content on the delay period for equivalent mixtures of carbon monoxide and oxygen at atmospheric pressure.

vapor is reduced in equivalent mixtures of carbon monoxide and oxygen, initially at atmospheric pressure. Reducing the pressure at constant water-vapor concentration also increases the delay markedly, but quantitative measurements

are difficult because of the decrease in the actinic light emitted by the explosions.

The real significance of the delay period is not known. It is possible that the low initial speeds of flame in space result chiefly from subnormal values of E , which in turn may be associated with the establishment of an equilibrium depth and structure of the reaction zone. If the normal reaction zone has a considerable depth, the flame front must travel at least this same distance from the point of ignition before the equilibrium structure is established. Previous to the attainment of such an equilibrium state, both S_t and E may be abnormally low and increasing toward their normal values.

Proposed Experimental Method. While flame records obtained in constant-volume bombs yield, directly, values of the speed of flame in space, means for measuring the rise in pressure must be provided if values of transformation velocity are to be obtained. Lewis and von Elbe⁴ have derived values of this property for ozone explosions from time-pressure records alone. However, if experimental records of both flame travel and pressure development are obtained, the observed quantities can be reduced to the desired properties in a simpler and more positive manner. A spherical bomb and auxiliary equipment designed to yield these two records simultaneously have been constructed at the National Bureau of Standards.

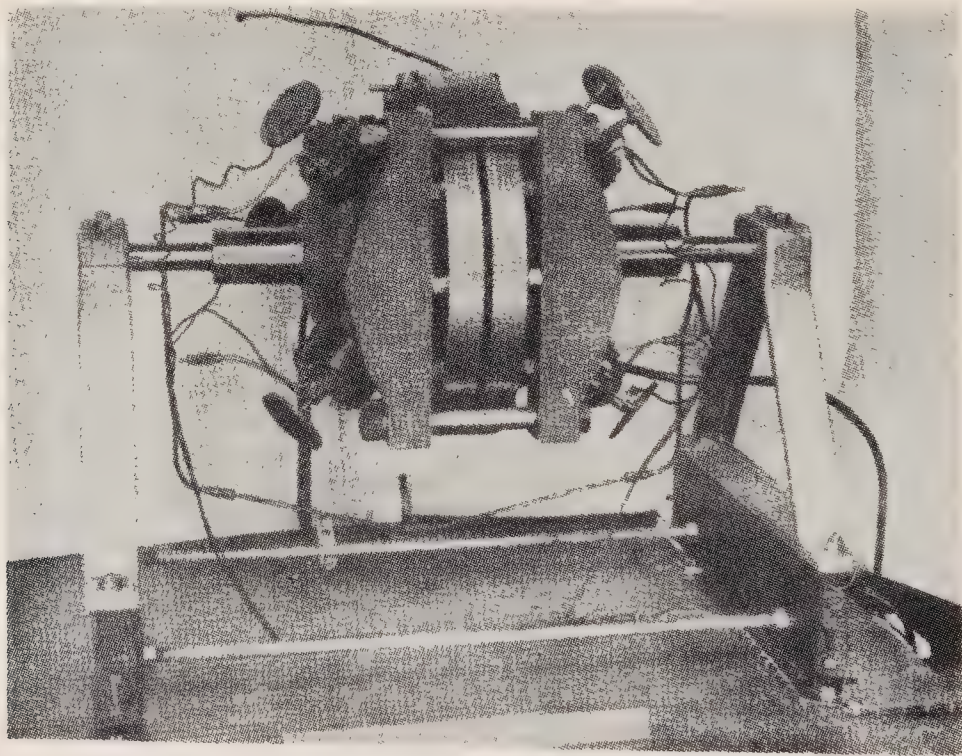


FIG. 11. Spherical steel bomb equipped to yield simultaneous records of flame travel and pressure development.

This bomb, shown in Fig. 11, is composed of two flanged hemispheres of stainless steel, clamped together upon a short cylindrical ring of glass. It is mounted with a narrow window in the vertical position so that the presence or absence of convective rise during burning may be detected. The spread of flame from the central point of ignition is photographed on a rotating film as in the bubble experiments. Six diaphragm indicators are provided to measure the rise in pressure which is recorded on the film with the flame trace.

Figure 12 is a diagrammatic representation of the spherical bomb with its window, and includes a comparison of typical flame traces for bomb and soap bubble.

When a spark occurs at the center of the bomb, a sphere of flame starts to spread exactly as in the constant-pressure explosion. However, the walls of the bomb soon resist the outward flow of gas set up by the expansion, and the unburned charge is compressed instead of merely being moved away by the advancing flame front. Thus the expanding gases cannot push the flame front outward as fast or as far as in the bubble explosion. As a result of the steadily decreasing outward gas velocity, the flame front travels more slowly as it approaches the walls, even though it may be propagating into the compressed and heated unburned charge at an ever-increasing speed.

The slopes of the flame traces shown in Fig. 12 constitute a direct measure of the speeds of flame in space. The slope of the trace of the flame in the bomb gradually decreases from the constant value of that in the bubble until it reaches a value at the wall which is a measure of the transformation velocity of the last portion of the charge to burn. This condition must always prevail since the last of the gas to burn cannot move beyond the walls, and is, therefore, essentially at rest when traversed by the flame.

Consider, as illustrated in Fig. 13, that the

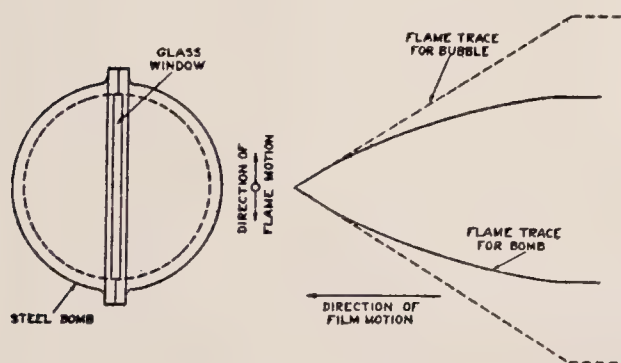


FIG. 12. Comparison of flame records obtained in the bomb and bubble methods.

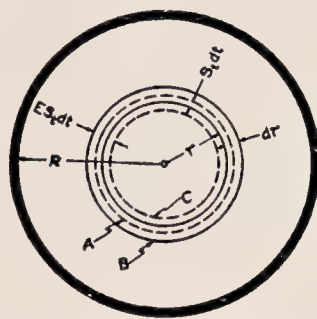


FIG. 13. Diagrammatic section indicating the significance of mathematical terms.

flame front, in a spherical bomb of radius R , has a radius r at time t after ignition. In the next increment of time dt , the reaction zone will transform a shell of gas of thickness $S_t dt$, which, upon expansion, will advance the flame front a total distance $dr = S_s dt$. Thus the remaining unburned gas is compressed from an inner boundary represented by the dotted line A to one represented by the solid line B , with an accompanying rise dp in pressure.

Applying the adiabatic law in differential form to this compression of the unburned charge gives

$$\frac{dp}{p} = \frac{-k_u dV_u}{V_u} = \frac{-3k_u r^2 (S_t dt - dr)}{R^3 - r^3}, \quad (5)$$

in which k is the adiabatic exponent, V is total volume, and the subscript u refers to the unburned gas.

Equation (5) reduces to the form

$$S_t = S_s - \frac{(R^3 - r^3)}{3pk_u r^2} \frac{dp}{dt}. \quad (6)$$

If E is the expansion ratio at time t and pressure p , the shell of unburned gas of thickness $S_t dt$ will expand, upon burning, to a volume of $4\pi r^2 E S_t dt$, compressing the previously burned gas to an outer boundary represented by dotted line C in Fig. 13. The observed increase in total volume of the burned gas is only $4\pi r^2 dr$, and the actual change in volume of the previously burned gas is therefore the difference

$$4\pi r^2 (dr - E S_t dt).$$

Applying the adiabatic law now to the compression of the previously burned gas, using the subscript b to designate properties of gas in this state,

$$\frac{dp}{p} = \frac{-k_b dV_b}{V_b} = \frac{3k_b (E S_t dt - dr)}{r}, \quad (7)$$

which reduces to

$$E = \frac{1}{S_t} \left[\frac{r}{3pk_b} \frac{dp}{dt} + S_s \right]. \quad (8)$$

The recompression of the burned gas by the subsequent expansion of surrounding layers is complicated by the shifts in equilibrium that accompany the compression and by the existence of both temperature and concentration gradients. When the burning has progressed to the stage where these effects are no longer negligible, it is difficult, if not impossible, to fix upon a value of k_b which will accurately represent the compression of the burned gases. However, the value of k_b has only a small effect upon the calculated value of E for the early stages of the explosion. Thus reliable values of E at the initial condition may be had, even though the selected value of k_b is somewhat uncertain. When the dissociation is negligible or calculable, the temperature, density, and concentration gradients which exist in the burned gas may be evaluated by a method such as that developed by Mache⁵ and applied by Lewis and von Elbe⁴ in obtaining numerical results for ozone-oxygen explosions.

The quantity dp/dt may be eliminated from Eqs. (6) and (8), yielding the equation

$$ES_t = S_s + \frac{k_u r^3}{k_b} \frac{(S_t - S_s)}{(R^3 - r^3)}. \quad (9)$$

If the explosion takes place at constant pressure, R is infinite and Eq. (9) reduces to $ES_t = S_s$, which is the relation [Eq. (3)] used in calculating S_t from the bubble experiments.

The conditions existing in the unburned gas at any instant may be calculated from the observed value of pressure, through the adiabatic law. From the experimentally determined variations of pressure and flame radius with time, values of the slopes $dr/dt = S_s$ and dp/dt may be found for any value of p , r , or t during an ex-

plosion at constant volume. Accurate values of k_u are available in the literature.

During an explosion at constant volume there will be a loss of heat from the layer of unburned gas nearest the walls of the bomb, tending to cause an ever-increasing departure from adiabatic compression as the temperature, density, and fraction of the remaining unburned gas in contact with the walls increase. On the other hand, the unburned gas may absorb some of the radiant energy from the flame, either directly or after it is reflected from the polished walls of the bomb. In the final stages of the explosion, preflame reactions may supply heat to the unburned charge. Since the total time of burning is very short, these effects are probably very small individually, and since they are not all in the same direction, their net effect will also be small. Certainly they may be ignored during the earlier stages of the explosion when temperature rises very little.

It is only during the very late stages of the burning that the temperature and pressure of the unburned gas change greatly. Here the departures from true adiabatic compression undoubtedly become appreciable, and the temperature of the unburned gas, as calculated from the observed pressure, is far less certain. Despite this fact, it is evident from Eq. (6) that the calculated values of S_t do not decrease in accuracy, because the term

$$\frac{(R^3 - r^3)}{3pk_u r^2} \frac{dp}{dt}$$

assumes a rapidly diminishing importance as r approaches R .

Some very short but finite time will elapse before the rise in pressure, that starts at ignition,

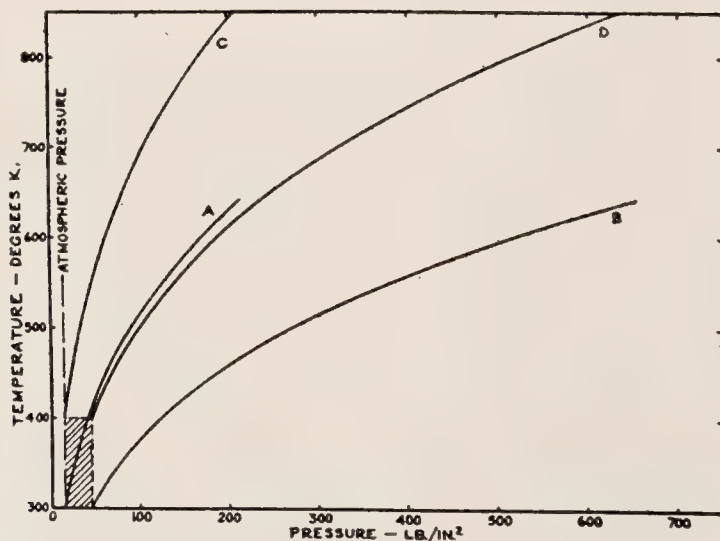


FIG. 14. Simultaneous rise in temperature and pressure resulting from the adiabatic compression of an equivalent mixture of carbon monoxide and oxygen from various initial states.

reaches pressure indicators at the walls of the bomb. During this brief interval there will be no recorded rise in pressure, the experimental values of dp/dt will be zero, and the value of S_t calculated by Eq. (6) will be identical with S_s , which is, of course, absurd. However, when the flame speed is well below the velocity of sound, the pressure gradients in the bomb are extremely small and soon become a negligible portion of the pressure rise, whereupon Eq. (6) becomes valid. Since it appears probable that errors due to non-uniformity of pressure will become negligible before the rise in pressure and temperature of the unburned charge is sufficient to cause significant change in S_t and E , there should be no necessity for attempting to evaluate the very early portion of the pressure curve.

Although the separate effects of charge temperature and pressure cannot be isolated from data on a single explosion, this may be done over a comparatively wide range by varying the initial conditions over a much smaller range.

Curve A of Fig. 14 shows the simultaneous rise in temperature and pressure of the unburned gas due to compression by the flame of an equivalent mixture of carbon monoxide and oxygen, originally at 300°K and 1 atm. If the initial temperature is maintained at 300°K and the pressure is varied between 1 and 3 atm, the range between curves A and B can be studied without special temperature control. If the initial temperature is 400°K, a pressure variation of from 1 to 3 atm permits study of the range between curves C and D. Thus by varying the initial temperature and pressure in the comparatively

small range indicated by the shaded rectangle, the entire region between B and C may be investigated. Since most points in this region may be reached from two or more different initial states, opportunity for correlating results at different stages of the explosion is provided.

Pressure Measurement. The utility of time-pressure records of explosions at constant volume has already been cited. Since the accuracy of the derived values of transformation velocity depends, among other things, upon that of the pressure measurements, these will be discussed briefly by referring to the method which is being used at the National Bureau of Standards.

Figure 15 shows calculated time-displacement and time-pressure records for an explosion in a spherical bomb of an equivalent mixture of carbon monoxide and oxygen, initially at 300°K and 1 atm. It will be noted that the pressure rises only about 0.2 atm while the flame traverses half the distance to the wall, and that it rises by about 14 atm during the last tenth of the travel. To obtain accurate results for the entire explosion it is necessary to measure accurately both the very small rise in pressure during the early stages and the high and rapidly rising pressure near the end.

The diaphragm type of pressure indicator was selected for its inherent simplicity, adaptability, and high precision. Preliminary experiments indicated that any sort of passage between the explosion chamber and the diaphragm of the indicator, even a well-perforated backing plate, is undesirable where high precision is required

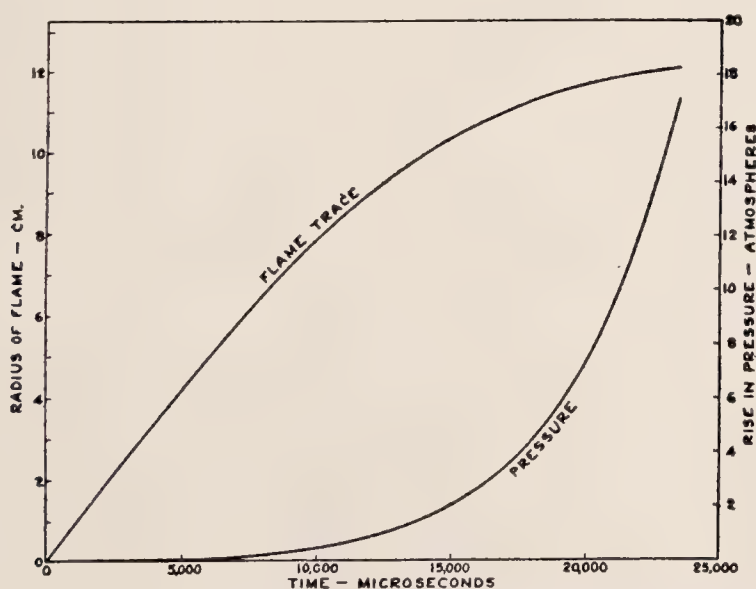


FIG. 15. Calculated time-displacement and time-pressure curves for the explosion of an equivalent mixture of carbon monoxide and oxygen in a spherical bomb of radius 12.2 cm. ($H_2O = 2.69$ per cent.)

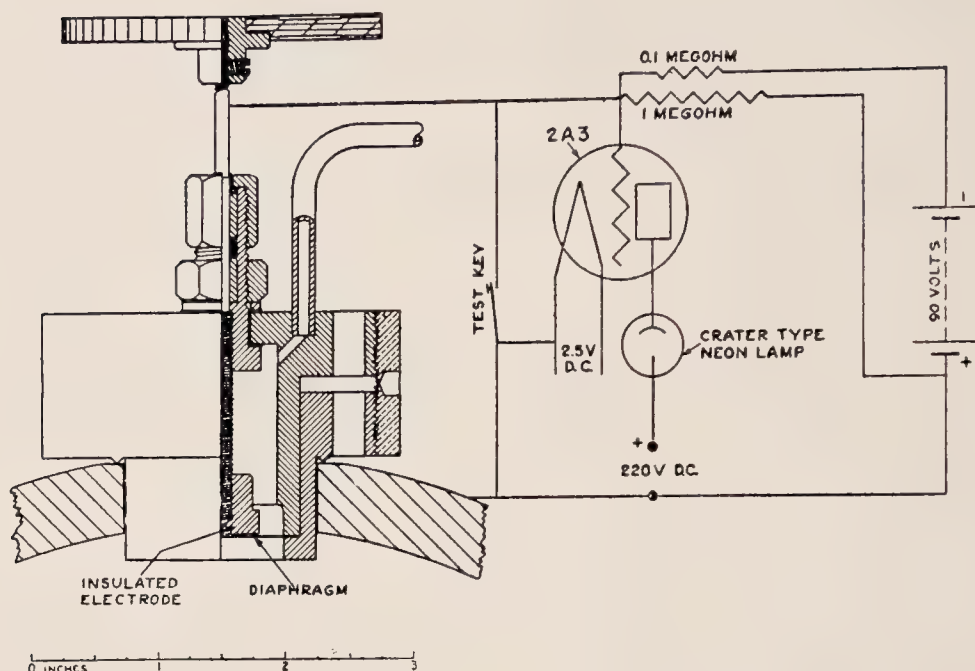


FIG. 16. Diaphragm pressure indicator, with recording circuit and lamp, designed for use with spherical bomb.

and fast-burning mixtures of high energy content are used.

The indicator, as shown in Fig. 16, is therefore constructed so that the diaphragm forms part of the combustion chamber wall. An insulated electrode can be adjusted to make contact with the diaphragm when the pressure in the bomb has reached any desired value. When contact is made, the negative bias on a vacuum tube (2A3) acting as a relay is reduced, permitting a larger current to flow through the plate circuit of the tube and a crater-type neon lamp. The lamp has a negligible time lag and may be readily photographed on the same film with the flame trace. A record is thus obtained of the instant that the predetermined pressure is attained in the bomb. Six similar indicators provide for recording six points on the time-pressure curve for each explosion, and several explosions from identical initial conditions will be required to establish the entire pressure curve.

In an indicator of the type shown in Fig. 16, the diaphragm need be only strong enough to withstand the pressure to be measured, for it is supported by the electrode after contact is made. The space behind the diaphragm is normally open to the atmosphere, and the diaphragm makes contact after being deflected elastically by the pressure in the bomb. However, the space behind the diaphragm may be sealed if desired and a backing pressure applied to give the diaphragm an initial deflection into the bomb. If the electrode has been previously set to make contact when the diaphragm returns to its neutral

position, the indicator will record the instant at which the pressure in the bomb is equal to the known constant backing pressure. In either case, the indicator may be calibrated in place, just before use, by setting the electrode, slowly increasing the pressure in the bomb until contact occurs, and measuring the pressure.

The only sources of significant error in an indicator of this type are variations in the static pressure required to cause contact on repeated trials and excessive inertia of the diaphragm, which would cause it to assume different positions under static and dynamic conditions. Preliminary tests with the six indicators mounted in the spherical bomb are being conducted to determine the diaphragm dimensions required for adequate strength and a satisfactory compromise between high reproducibility and low inertia error in different portions of the pressure range.

Conclusions

To be of greatest usefulness, a method for measuring flame speed must yield values of transformation velocity, which is the speed of flame in a direction normal to its surface and relative to the unburned charge. Of the various methods which have been used, those employing spherical flames are probably susceptible of the most rigorous analysis. Transformation velocities may be determined for explosions producing spherical flames either at constant pressure or at constant volume.

In both methods adequate control of the com-

position of the mixtures must be provided and all components must be gases or vapors. The light emitted by the explosions must be sufficiently actinic for photographic purposes. Flame speeds must not be so high that excessive pressure gradients are developed ahead of the flame front, or so low that convective rise is apparent during the explosion. Each method has, in addition, its individual advantages and limitations.

The constant-pressure or bubble method for measuring flame speeds has the great advantage that it requires the measurement neither of rapidly changing pressure nor of gas flow. All results are derived from a simple photographic record of flame spread which is rapidly obtained and easily analyzed. The value of the speed of flame in space as obtained by this method is a characteristic property of the explosive mixture dependent only upon its transformation velocity and expansion ratio. Under favorable conditions all three of these properties can be evaluated by the bubble method, with a precision which is probably equal or superior to that attainable by any other method.

The principal disadvantage of the bubble method is that the partial pressure of water vapor in the explosive mixture is fixed by the temperature and composition of the soap film. It is therefore not practicable to maintain the temperature constant while the effect of variation in water vapor content is studied, or to maintain a constant ratio of moisture to active charge while temperature, pressure, and extent of dilution by inert gases are varied independently. This limitation is especially serious when the water is involved in the combustion reactions, as in mixtures of carbon monoxide and oxygen.

Materials of the soap film must not react with or dissolve any constituent of the explosive mixture and thus cause significant changes in its composition. In very rich mixtures the excess fuel burns in the surrounding atmosphere after the flame front has completely traversed the original mixture. In such cases values of transformation velocity and expansion ratio cannot be determined.

The spherical bomb of constant volume is adapted to the measurement of flame speeds over much wider ranges of charge composition, pressure, and temperature than is feasible with the bubble method. Charge composition may be varied at will, so long as all constituents are gases or vapors. The independent effects of pressure and temperature upon flame speeds may be isolated over a considerable range by making relatively small changes in initial pressure only, and the range may be greatly extended if provision is made for moderate variation of initial temperature. Conditions in the spherical bomb may

thus be made to approach those prevailing in an engine, but greater opportunity exists for independent variation and control of conditions.

The gross mechanism of an explosion at constant volume is much more complex than for one at constant pressure, a more complicated apparatus and procedure are required for the determination of transformation velocity, and there is greater opportunity for error in the results. Perhaps the greatest single difficulty is in the accurate measurement of pressure. Indicators should be capable of recording faithfully both the very small initial rise in pressure during the early stages of the explosion and the high and rapidly rising pressures near the end. The necessity for evaluating slopes of the flame-travel and pressure-development curves involves errors which vary in magnitude with the position of the flame front. Greatest error in the results would be expected in the very early and very late stages.

It is hoped that future measurements of flame speed, through further development and use of both methods, will provide basic information which will clarify the mechanism of flame propagation and suggest practical means for further control of gaseous explosions. It is believed that such studies will yield results of many types, any or all of which may contribute to our knowledge of the combustion process and aid in its further improvement as a source of power in engines.

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PROBLEMS OF STATIONARY FLAMES*

FRANCIS A. SMITH

National Bureau of Standards, U.S. Department of Commerce, Washington, D. C.

I. Introduction

It is the purpose of this paper to present, semi-quantitatively, a number of the problems involved in the measurement of flame speeds by burner methods, and some fundamental problems connected with the utilization of stationary flames by means of burners of several kinds. Since the burner is the control device by means of which the flame is made to function, the problems and uses of stationary flames are bound up inextricably with it. Of the various factors to be considered in the manipulation of stationary flames, it is becoming increasingly apparent that flame speed plays the dominant role and that it usually appears as the determining factor in the behavior of the flame.

It is unfortunate that burner methods of measuring flame speeds appear to be reliable within only a limited range of operating conditions. The methods are relatively simple, and within their limitations the results apply directly to a multitude of problems involving flames and burners. Some of these problems are presented very briefly, merely for illustration and without any attempt at exhaustive treatment.

II. Flame Speeds by Burner Methods

A. Brief Review of Methods of Measurement and Computation

When measurements of flame speed were first undertaken by burner methods, Bunsen³ assumed that the downward velocity of the flame front just exceeded the upward velocity of the gas mixture at the moment when the flame flashed back down the burner tube. Obviously this could be true only if the velocity were uniform across the stream of gas mixture.

Gouy⁷ at first considered the flame speed to be equal to the product of the velocity of the gas mixture and the sine of the angle which the side of the flame cone made with its axis. Then, finding that the surface formed by the flame front did not approximate sufficiently to a true cone (see Fig. 1) and that the result obtained depended upon what part of the flame front he used when he measured the angle, he eliminated the angle from consideration by setting the velocity of the flame equal to the volumetric

rate of flow of the mixture divided by the area of the flame surface. This involves the concept of flame speed as simply the rate of transformation of the mixture, without the necessity of considering the velocity of the gas mixture and its direction of flow. The two concepts would yield identical results if the flame surface were a geometrical cone with the burner port for a base.

Gouy determined the area of the flame surface from measurements of the image of the flame projected on a screen. Considering the figure as a surface of revolution, he obtained the area by integration.

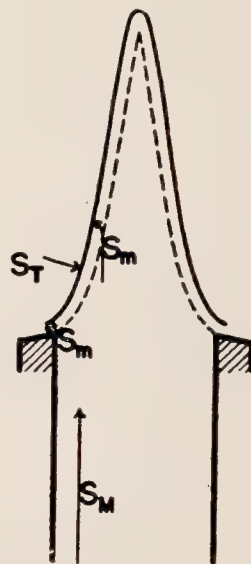


FIG. 1. Shape of typical flame surface.

Michelson⁸ also measured the volumetric rate of flow of the mixture and determined the actual area of the "cone" by treating measurements of enlarged photographs in the same way that Gouy had done.

Ubbelohde and Koelliker¹⁵ concluded that the rounded tip and the curved base of the flame surface represented deviations from what they termed the "normal" flame velocity, so they measured the angle made by the "straight" portion of the flame surface with its axis, and computed the result as Gouy had done originally.

Stevens¹³ was unable to obtain results with the burner which were in satisfactory agreement with the results he obtained with the "bubble" when he determined the area of a flame surface as Gouy, Michelson, or Ubbelohde had done. He recognized, as did Ubbelohde, that the approximately conical flame surface was the resultant of several components, one of which was a mixture

* Publication approved by the Director of the National Bureau of Standards of the U.S. Department of Commerce.

velocity which varied from practically zero at the walls of the burner tube to a maximum at the center. Stevens, therefore, made use of only that part of the flame surface which resulted from the portion of gas mixture whose actual linear velocity was equal to the mean velocity over the cross section of the stream. He constructed on the photograph of a flame a triangle having as its base the diameter of the burner port and its sides parallel to the tangents to the flame surface at the part where the velocity of the mixture equaled the mean velocity. Considering this triangle as a section through the axis of a cone, the area of the cone was easily calculated without integration from the measured altitude and base, and values obtained from it for the velocity of the flame front relative to mixtures of carbon monoxide and oxygen agreed with those obtained with the bubble so closely that the two methods, for many purposes, could be used interchangeably.

A number of other workers have adhered to Gouy's assumption, expressing flame speed in terms of volume of combustible mixture per second divided by the area of the flame surface. Of these, some use the actual integrated area of the flame surface and others use the area of a geometrical cone having the burner port as a base. The area of this geometrical cone has been arrived at in various ways, which have no bearing on what follows and will not be discussed here.

Since the area of the burner port divided by the lateral area of a geometrical cone of which the burner port forms the base is equal to $\sin \alpha$ (where α is the angle between the side and the axis of the cone), the cone may also be defined by the area of the burner port and the angle α . All of these expressions would lead to the same numerical result were the flame surface a geometrical cone.

Instead of measuring and computing the area of the cone as Stevens had done, Smith and Pickering¹² chose to measure directly the angle α between the tangents and the axis, which, together with the burner port, is sufficient to define the cone. Instead of dividing the volumetric rate of flow of the combustible mixture by the area of the cone to obtain the flame speed, the rate was divided by the area of the burner port, thus obtaining the average linear velocity of flow of the mixture. The angle was measured, with the instrument shown in Fig. 2, at that part of the flame surface where the local velocity of flow of the mixture was equal to the average velocity, i.e., at a point $0.7r$ from the axis. The sine of the angle α , multiplied by the average velocity of the mixture (S_M), then gave the same numerical value for the flame speed (S_T) as did Stevens' method. The velocity of propagation of the flame front, in a direction normal to its surface and relative to the combustible mixture in which it moves, was then given by the equation $S_T = S_M \sin \alpha$.

B. The Influence of Several Experimental Factors on the Numerical Result for the Flame Speed

In any combustible mixture of gases of given composition, temperature, and pressure, there is a definite fixed value for the flame speed relative to the gas mixture. Consequently, if different values are obtained by different means, it must be concluded either that one of the supposedly fixed experimental conditions was not what it was supposed to be, or that the differences in the numerical result have been imposed by differences in the methods of measurement and computation, or by the apparatus.

On this basis the degree to which the numerical

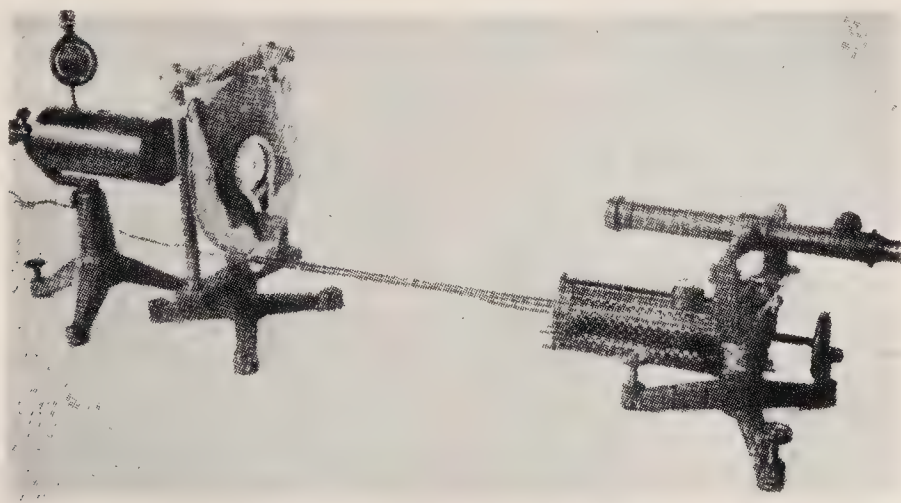


FIG. 2. Goniometer and reading telescope for measuring the angle between the two sides of the flame surface.

TABLE I
Effect on S_T of changing the velocity of
the same mixture

Gas in mixture, %	Velocity of mixture, cm/sec S_M	Flame speed, cm/sec $S_T = S_M \sin \alpha$
(A) 9.60-mm burner. Propane-air		
4.76	64.4	33.9
4.69	87.2	34.5
4.59	111.7	33.9
4.54	131.2	33.5
4.41	155.9	34.3
4.38	178.4	32.7
(B) 2.75-mm burner. City gas-air		
17.55	221.7	46.3
17.56	209.4	47.2
17.48	193.3	47.2
17.47	171.3	46.0
17.57	150.4	46.6
17.53	128.8	47.9

result is found to be independent of the method or apparatus for obtaining it may be used as a criterion of the extent to which that result approaches the supposedly correct definite fixed value assumed above to exist.

1. *The Numerical Result is Independent of the Velocity of Flow of the Mixture, So Long as the Flow is Laminar.* With a given combustible mixture, a high velocity of flow from the port results in a long narrow flame and *vice versa*. The results presented in Table I show that, all other conditions remaining substantially constant, the flame speed S_T is unaffected by changes in the mixture velocity which range from incipient flashing back to incipient blowing off of the flame.

Ubbelohde and Koelliker¹⁵ studied the effect with mixtures of hydrogen and air. The maximum-speed mixtures showed the same flame speed until the mixture velocity reached 1300 cm per second, which corresponds to a Reynolds number, R , of over 2400. [$R = DVd/\mu$, where D = diameter of burner tube expressed in cm, V = velocity of fluid in cm/sec, d = density of fluid in g/cm³, and μ = viscosity of fluid in c.g.s. units.] Since at the critical velocity $R = 2300$, the flow was probably no longer laminar but turbulent. This undoubtedly accounts for the increased value of the flame speed which they found at higher velocities.

2. *The Result Depends Upon the Size of the Port, Especially if the Area of the Flame is Used in Obtaining the Result.* Several workers, including Ubbelohde and Koelliker,¹⁵ have concluded that burners of different sizes yield different results. Ubbelohde and Hofsäss¹⁴ state that the error is larger with small burners and both agree that it tends to disappear as the composition of the mixture approaches that for maximum flame speed. Corsiglia,⁴ however, states that different sizes of burners yield the same result within the limit of experimental error. Smith and Pickering,¹² for comparison, computed the flame speed from measurements of twelve flames by the method of Corsiglia as well as by their own.

Figure 3 shows curves representing the flame speed in each of three mixtures. Set A contained 62 per cent of the air required for complete combustion of the gas, Set B 90 per cent (maximum S_T), and Set C 103 per cent. Each mixture was used with four burners having internal diameters of 2.75, 4.45, 6.50, and 9.60 mm, respectively. Within each set the value of S_M , as well as the temperature and composition of the mixture, was kept constant as the size of the port was changed.

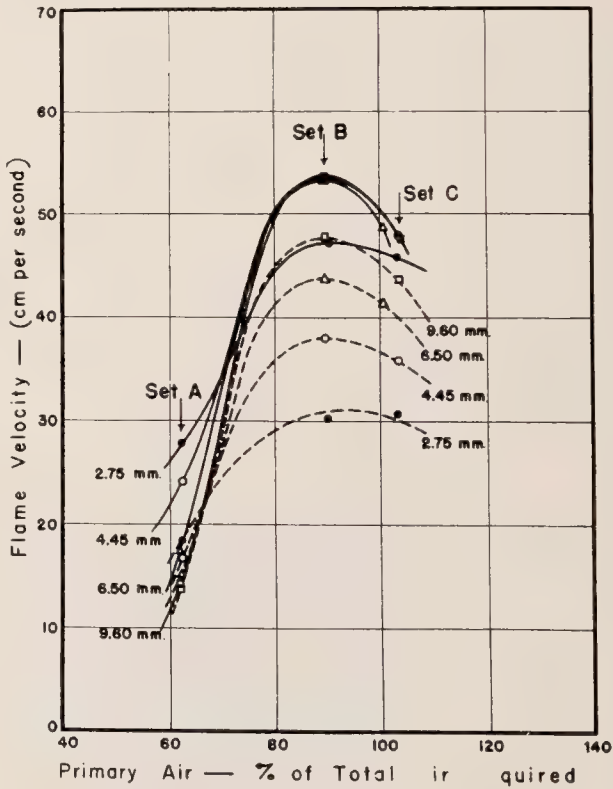


FIG. 3. Flame-speed curves. Composition, temperature, pressure, and S_M constant within each set. The solid curves result from measurements of the angle. The dotted curves result from measurements of the area of the flame surface by the method of Corsiglia.

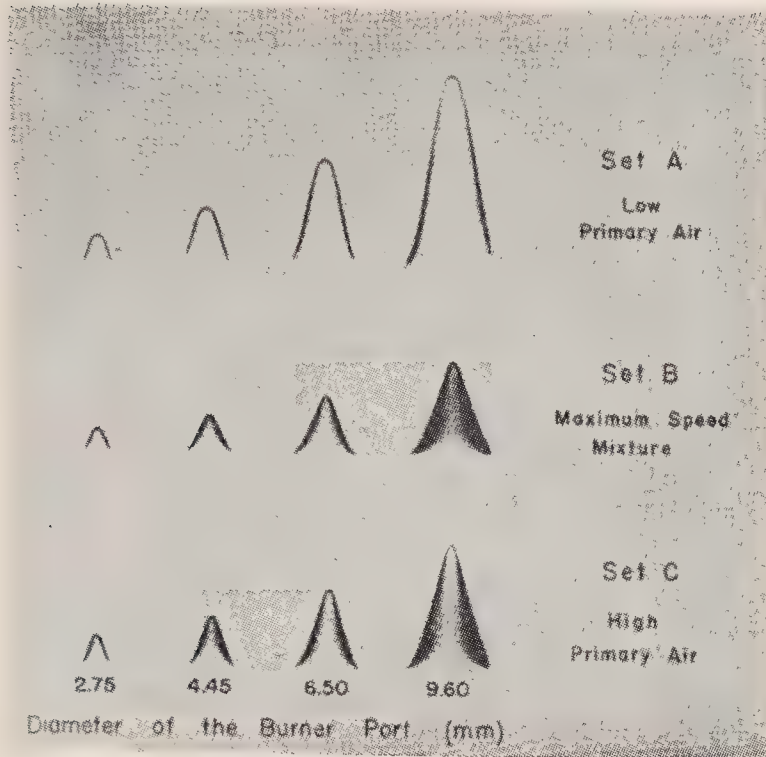


FIG. 4. Relative sizes and shapes of flames on four burners of different diameters when temperature, pressure, composition, and S_M were kept constant within each set.

The solid curves result from measurements of the angle by the method of Smith and Pickering.¹² With the maximum-speed mixture, the same result is obtained on the three larger burners, within the limit of experimental error. The 2.75-mm burner is about 11 per cent lower. In the other mixtures, especially in Set A with the low primary air, the results with the different burners are widely divergent. The broken curves result from measurements of the area of the flame surface, on the same photographs, by the method of Corsiglia.⁴ The results from the different burners are widely divergent in the maximum-speed mixture, but agree very well at about 67 per cent of the total air required. The reasons for such divergent results will be apparent from the next two figures.

Figure 4 shows the four flames of each set and the relative sizes and shapes which result when S_M and composition are kept constant within each set.

Figure 5 shows the same flames with the four burners of each set enlarged by the proper amount to give each burner port the same apparent diameter. The position of the port with respect to the flame is indicated by the horizontal line under each flame. Since the composition and temperature of the mixture were kept constant, the product $S_M \sin \alpha$ is fixed within each set. In

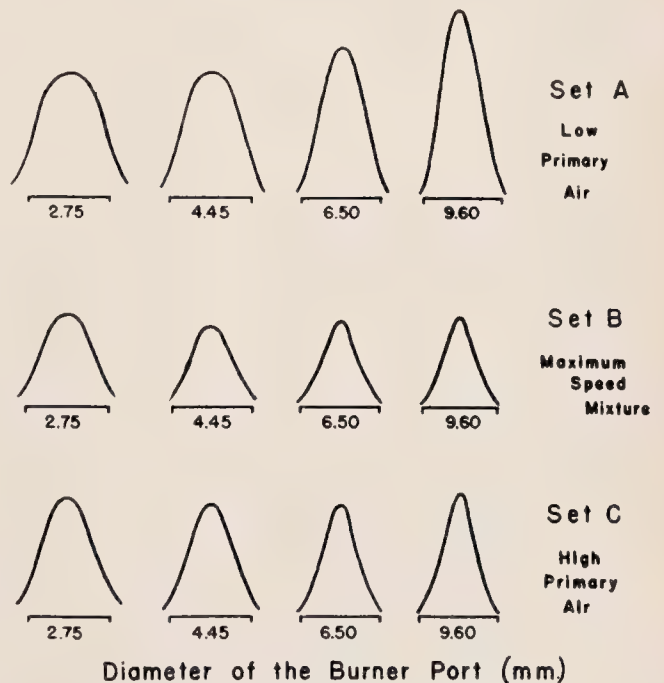


FIG. 5. Effect of burners of different sizes on the shape of the flame surface. Tracings of the flames of Fig. 4 with the four burners of each set enlarged by different amounts to give each burner port the same apparent diameter, the position of which with respect to the flame is indicated by the horizontal lines under the flames.

TABLE II

Effect of changes of port diameter upon the angle α , and consequently upon the numerical value of flame speed as calculated from measurements of the angle

Port diameter, mm	Composition of mixture, per cent primary air	Velocity of mixture, S_M , cm/sec	Angle α	Flame speed $S_M \sin \alpha$, cm/sec
Set A. Low primary air				
2.75	62.3	85.4	19° 5'	27.9
4.45	62.3	85.2	16° 32'	24.2
6.50	62.0	85.1	11° 48'	17.4
9.60	61.9	85.2	9° 43'	14.4
Set B. Maximum-speed mixture				
2.75	90.4	121.0	22° 58'	47.2
4.45	89.6	120.2	26° 27'	53.5
6.50	89.6	120.4	26° 19'	53.4
9.60	89.6	120.7	26° 36'	53.7
Set C. High primary air				
2.75	103.2	140.2	19° 4'	45.8
4.45	103.5	140.0	20° 8'	48.2
6.50	100.7	140.8	20° 13'	48.7
9.60	103.7	140.3	20° 3'	48.1

addition S_M was also kept constant, thus concentrating any differences between flames of different size in the angle α .

Table II shows that for the three larger burners in Sets B and C the angle, and consequently the flame speed, is practically constant and independent of the size of the port.

Likewise, keeping all conditions constant except port size, any differences resulting from ports of different sizes are concentrated in the areas of the flame surfaces. Such differences are obvious in Fig. 5, especially in the case of Set A and the smallest burner of all three sets.

Table III presents the enlarged areas, measured by the method described by Corsiglia. These show clearly that the area is not independent of the size of the port. Consequently, the flame speed, computed from the volumetric rate and the actual area of the flame surface, is dependent on the size of the port.

3. *Computations of Flame Speed. Angle Measurements Versus Area Measurements.* Table IV shows the results of computing the flame speed, in these

two ways, from measurements of the same flames. On the basis of our assumption of a definite fixed flame speed corresponding to a fixed composition and temperature of the combustible mixture, the results based on the angle appear to be a more reliable index to flame speed than those based on the area, for the case of burners larger than about 4 mm in diameter and at or near the maximum-speed mixture. The values from the area are lower than, and appear to approach, those from the angle, and might reach coincidence if a burner of larger size were used. This is indicated in Fig. 3, which also shows that at about 67 per cent of the total air required the results based on the area are independent of port size, and agree with that from the angle with the

TABLE III

Effect of changes in port diameter upon the area of the flame surface, and consequently upon the numerical value of flame speed calculated from measurements of the area. Composition of S_M constant in a given set

Port diameter, mm	Enlarged area*	Flame speed Volume rate/actual area cm/sec
Set A. Low primary air		
2.75	654.0	18.5
4.45	729.3	16.8
6.50	801.9	15.1
9.60	869.9	13.8
Set B. Maximum-speed mixture		
2.75	589.6	29.0
4.45	455.3	38.0
6.50	390.1	43.8
9.60	356.1	47.7
Set C. High primary air		
2.75	644.4	30.7
4.45	560.9	35.9
6.50	483.7	41.3
9.60	453.8	43.6

* The enlarged area is the area of the flame surface, in arbitrary units, measured after the flames have been brought to a common basis for comparison, by enlargement of all ports to the same apparent diameter. If changing the size of the port had no effect upon the shape of the flame, and if the flame base was congruent with the port, all four areas within a given set would be equal.

TABLE IV

Effect on the numerical value for flame speed of computations based on measurements of the angle, as compared with those based on measurements of the area, with changes of port diameter. Composition and S_M constant in a given set

Port diameter, mm	Flame speed $S_M \sin \alpha$ (cm/sec)	Flame speed Volume rate/actual area (cm/sec)
Set A. Low primary air		
2.75	27.9	18.5
4.45	24.2	16.8
6.50	17.4	15.1
9.60	14.4	13.8
Set B. Maximum-speed mixture		
2.75	47.2	29.6
4.45	53.5	38.0
6.50	53.4	43.8
9.60	53.6	47.7
Set C. High primary air		
2.75	45.8	30.7
4.45	48.2	35.9
6.50	48.7	41.3
9.60	48.1	43.6

9.60-mm burner. Whether any significance may be attached to this must await results by some such method as that described by Fiock and Marvin⁶ in another part of this symposium.

Such differences as are significant in the shape of the flame surface when the same mixture is burned on burners of different size and when different mixtures are burned on the same burner have long been noted and are brought out in Fig. 4. Measurements indicate that the base of the flame is, in most cases, about 1.0 mm larger in diameter than the port and somewhat above it. This, on a burner of 2.75-mm diameter, amounts to 36 per cent of the port diameter.

The incongruity between the base of the flame and the port and the rounding off of the top of the flame lead to an area larger than that of a geometrical cone having the port as a base. Consequently, the numerical result for flame speed is lower as the distortion in shape becomes greater.

The angle is apparently affected much less than the area by the relative changes of shape

and size which accompany changes in the size of the port.

4. *Maximum-Speed Mixtures Give Minimum Errors and Are Least Objectionable for Comparisons Between Fuel Gases.* It is clearly seen from Fig. 5 that the shape of the flames which yielded results least affected by changes in the size of the burner was that which departed least from the shape of a geometrical cone. This condition is found in or near maximum-speed mixtures and with the larger burners.

If the ability to measure the speed of flame relative to a combustible mixture is to be of any use whatever, one must be able to compare the speed in one mixture with that in another, and the speeds in mixtures of one fuel gas with those in mixtures of another. The limitations of the burner method of measuring flame speeds in regard to the former have just been considered.

A problem common to all methods is that of finding a suitable basis on which to make the comparison with respect to different fuel gases. For example, the data from the two gases may be obtained by the same method, with the same apparatus, and the comparison may be made (a) by substituting one combustible gas for the other in a gas-air mixture which is otherwise unchanged in composition and temperature. The two gases may be methane and propane, each constituting 7.5 per cent of its mixture with air. An examination of the curves plotted in Fig. 6 shows that all that can be elicited from such a comparison is that the flame velocity in a very lean mixture containing 7.5 per cent of methane is more than twice that in a very rich mixture containing 7.5 per cent of propane. The comparison may also be made (b) between mixtures, each of which contains the same percentage of the total air required for the complete combustion of the respective gases. The curves plotted in Fig. 7 show that such a comparison may be valid between methane and propane, but if either of the gases is compared with hydrogen in mixtures containing, for example, 80 per cent of the air required for complete combustion, the same difficulties are encountered as before but not to such an extreme degree. Such comparisons are obviously useless, and the alternative of choosing the maximum-speed mixtures as the only points on the curves which are much more than roughly comparable one with another must be accepted. Even with maximum-speed mixtures, the flame speeds in different mixtures, obtained by different methods, may be compared with validity only when the different methods have been shown to yield the same result with a given mixture, the composition, temperature, and pressure being the same in each case.

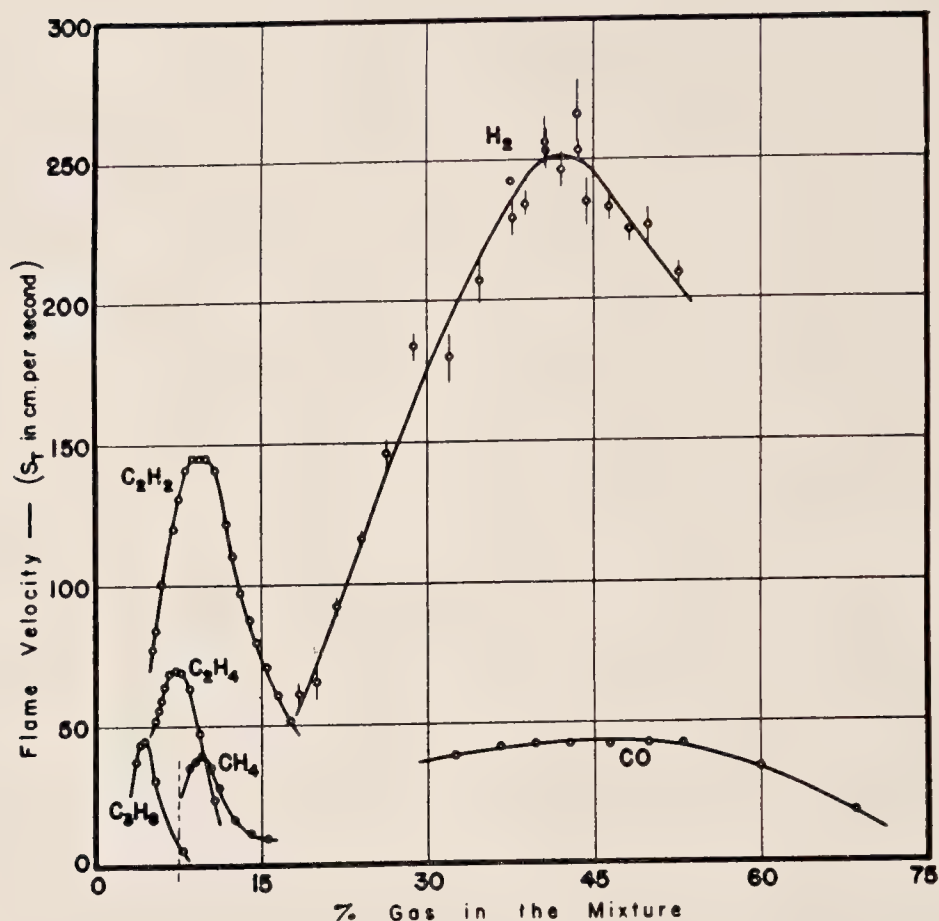


FIG. 6. Flame-speed curves plotted, in the customary manner, with "percentage of gas in the mixture" as abscissa

C. Changes in the Distribution of Velocities in a Stream of Mixture Emerging from a Burner Tube

Among the factors which influence the shape of the flame surface is the velocity of flow of the mixture. The surface of the flame may be considered to be generated by the movement of a flame front radially from a point of ignition on the outer boundary of the moving stream of mixture. If the velocity of the stream were uniform throughout, the flame front would be the surface of a segment of a sphere, all parts of which were being carried away from the burner port by the stream of mixture. If flame front and mixture traveled at the same speed, a nearly flat flame surface across the port would soon result. The spherical flame front would remain in contact with the port rim, at the original position of the point of ignition, its radius of curvature continually increasing as its center (the point of ignition) receded in the moving stream. Such a situation would probably be not far from the original conception of Bunsen, who assumed that the flame speed just exceeded the mixture velocity when the flame traveled down through

the port. Although it may be approached with ports about 4 mm in diameter or less at low rates of flow, this condition is never found in practice.

Theoretically, the distribution of velocities in a fluid in laminar flow in a tube is parabolic. This means that the maximum velocity at the axis is twice the average velocity, and that the average velocity occurs in a cylindrical lamina having a diameter 0.707 that of the tube. Ordinarily, the distribution is probably only approximately parabolic and the average velocity of the mixture is several times as great as the flame speed.

Some early workers in the field attempted to compute the changes in velocity in the various parts of such a stream of gas when it emerged from the tube into the surrounding air, but without success. They, and most others, have assumed that the parabolic distribution persists, without significant modification, for a sufficient distance from the port to include the inner cone of the flame.

In the course of the study of flames and burners at the National Bureau of Standards, interest in this matter was revived late in 1935 in an attempt to account for the marked rounding

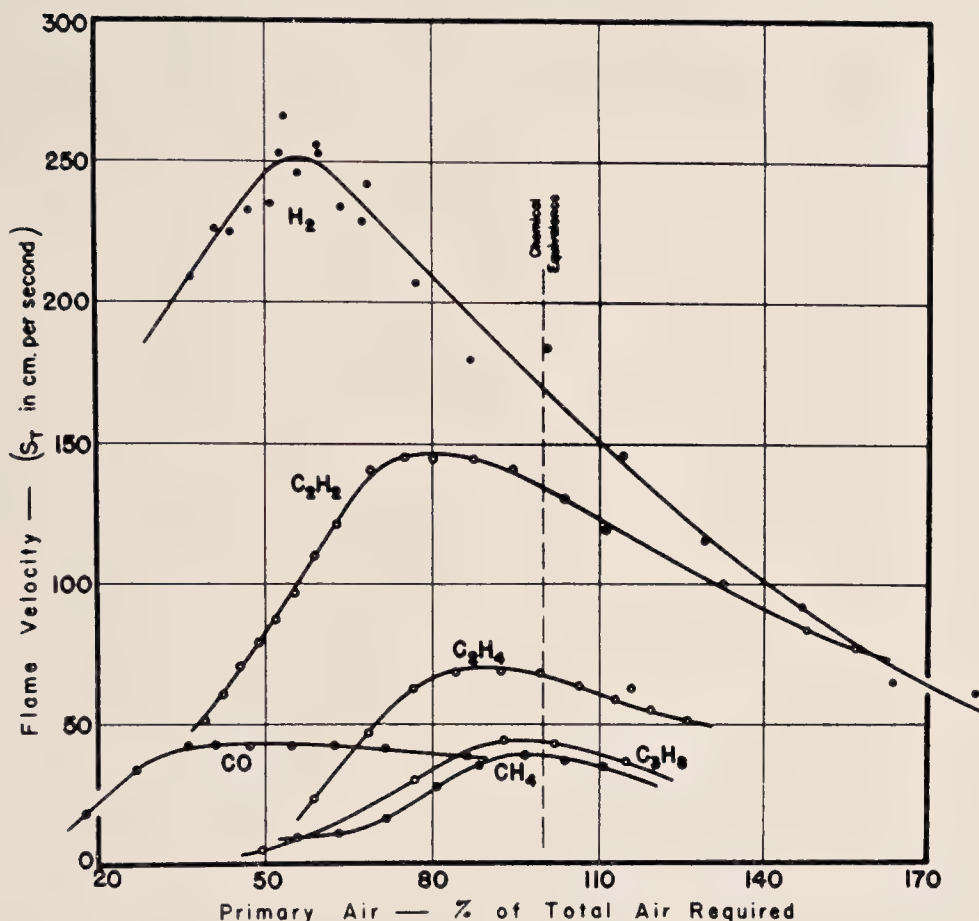


FIG. 7. Flame-speed curves plotted to place the gases on a common basis with respect to the air required for combustion, and nearly so with respect to heating value.

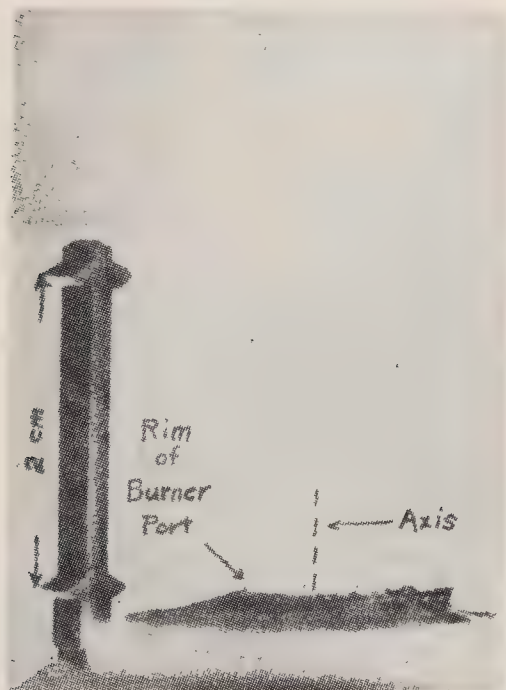


FIG. 8. Aluminum particles, suspended in a stream of air rising from a burner tube, photographed by reflected light, interrupted by a slotted disc rotating at known speed.

off of the tops of some of the flames which have just been discussed. Other widely scattered workers have also become interested.

Some preliminary work has been done by the writer in an attempt to detect and measure such a redistribution of velocities in the stream of the mixture by photographing particles of aluminum suspended in the stream. Fig. 8 shows a photograph, measurements of which indicate that there is a deceleration of particles near the axis and an acceleration of those near the boundaries of the stream. The velocity at points from 1 to 2.5 diameters above the port and near the axis was decreasing about 3.4 cm per second in 1 cm. At the same time the velocity at points from $\frac{1}{3}$ to 2 diameters above the port and near the boundaries of the stream was increasing about 11 cm per second in 1 cm on one side and from 8 to 50 cm per second in 1 cm on the other. Of course, the velocity at the boundaries was still only a fraction of that near the axis at these short distances from the port, but the measurements indicate that changes of considerable magnitude in the distribution of velocity were taking place within a relatively short distance from the port.

Predvoditelev and Stupotshenko¹¹ have studied

the problem of a decaying gas jet with pipes 100 mm in diameter and larger by means of an anemometer. Predvoditelev¹⁰ concludes that: "The inner cone of the Bunsen flame is a photograph of the hydrodynamic law of the distribution of velocities over the cross-section of the torch, nothing more." It seems certain that this is an overstatement of the case. Apparently he considers that the flame surface is farther from the port at the axis than it is at the boundaries of the stream, only because the velocity of flow of the mixture is greater at the axis than at the boundary. Smith and Pickering,¹² as well as various other workers, have shown that the angle between flame surface and axis depends on the ratio of flame speed to mixture velocity, and not on mixture velocity alone.

III. Problems of Stationary Flames as Related to Burners

A. Kinds of Stationary Flames

A stationary flame may be defined as one in which a stream of combustible material flows through a flame front maintained in a fixed position by some mechanical device usually called a burner.

Stationary flames may be classified in various ways, but for the purposes of this discussion the classification will be on the basis of whether or not part of the air required for combustion of the gas is mixed with it before it emerges from the port.

1. *Diffusion Flames.* In this classification fall all those flames in which the fuel gas emerges from the burner as and when it becomes mixed with a sufficient quantity of surrounding air. Such flames range from candle, wick lamp, gasoline flare, through the old gas light, the acetylene flashing beacon, some newer industrial equipment, to the old jewelers' blowpipe and modern blast lamp.

In all these the process of liberating heat is limited in speed by the rate at which mixing takes place between the gas and air. In some it is accomplished by diffusion alone. In some, mechanical mixing plays a relatively important part. In blowpipe and blast lamp mixing is accelerated by forcing a jet of air through the emerging gas. This not only increases the area of contact between gas and air, but produces considerable mixing by turbulence as well.

Such flames occupy a relatively large space compared to the rate at which they liberate heat, for the flame surface must extend itself until all the fuel gas has made contact with the air required to burn it.

2. *Bunsen-Type Flames.* To this class belong flames of almost all domestic gas appliances, many laboratory burners, many industrial and special purpose burners, blow torches, welding torches, etc., in which the fuel gas is mixed with a part or all of the air it requires for combustion before it emerges from the port. Many of these burners use part of the energy of the gas supplied to them under pressure to inject or inspire this primary air and assist in the mixing. Others have both gas and air supplied under pressure, and the mixture is controlled by means of valves.

In all these cases, however, the speed of the combustion process is limited by the speed at which flame travels relative to the particular mixture flowing from the port. It is with this class of flames that this discussion is primarily concerned.

B. Usefulness of Flames as Related to Stability

A flame is useful only so long as it remains on the burner. One may use the burner as a handle with which to change the size, direction, or intensity of the flame. Since usefulness depends on the flame remaining stable, subject to control by means of a burner under a variety of changes, problems of stationary flames are involved inextricably with those of burners.

The limits of the stable range of operation of a flame are evidenced by the flame flashing back inside the port at one extreme and being blown off the port by the stream of mixture at the other. Whether the flame operates near one of these limits or the other depends on the relative magnitudes of the flame speed, S_T , and the velocity of flow of the mixture under the varied conditions of use.

1. *Range of Variation of Velocity of Mixture of Constant Flame Speed.* When the proportions of fuel and air must be kept constant while the rate of heat production is varied, as is sometimes the case, the range of stable operation with a given burner is greatest when the proportion of primary air is least. As may be seen from Fig. 9, for the case of a burner port 6.50 mm in diameter burning city gas, mixtures containing less than 40 per cent of the air required for complete combustion of the gas are not likely to flash back until flow practically ceases. Likewise, a very rapid flow is required to blow the flame from the port. In the maximum-speed mixture, the range of stable operation between flash-back and blow-off is very much less, and, in mixtures containing as much as 150 per cent of the theoretically required air, one limit or the other is encountered if only a slight variation in the rate of heating is permitted. Furthermore, the rate of heating has

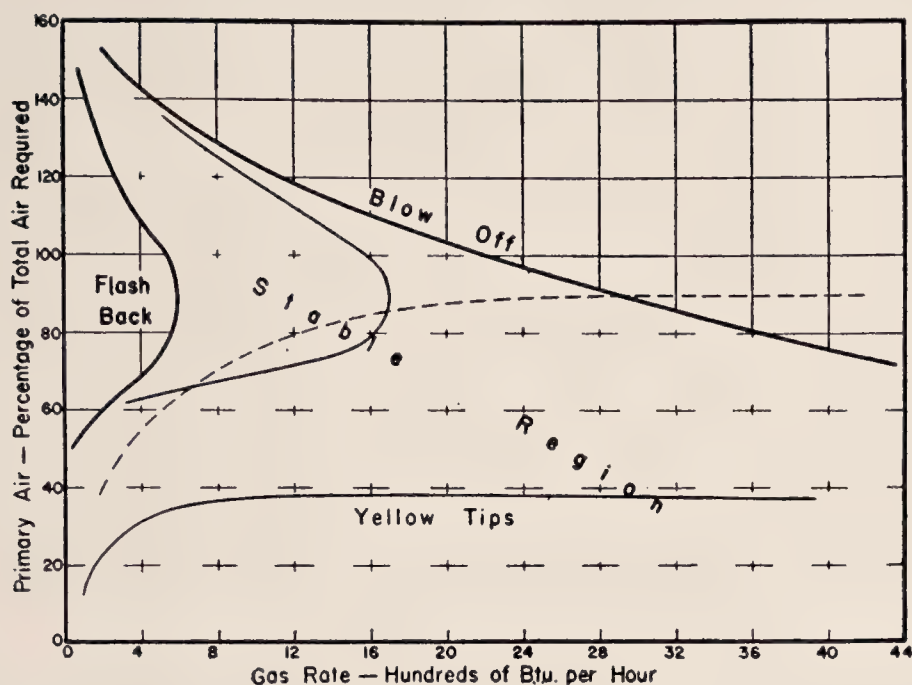


FIG. 9. Typical operation curves bounding the regions in which flash-back, blow-off, and yellow tips occur. The recurved blow-off curve results if secondary air is excluded. The dotted curve typifies the proportion of air injected by the gas. (6.50-mm burner with city gas-air.)

become so low as to be of little use. If the conditions of operation are such that the products of combustion, in escaping, exclude secondary air, the curve representing the blow-off limit doubles back toward the flash-back limit. The range of stable operation is then greatest in the maximum-speed mixture and decreases rapidly as the proportion of air is changed in either direction, with simultaneous reduction in the rate of heating.

2. Range of Variations in Composition. In most applications of gas flames the composition, as well as the velocity of the mixture, is subject to variation. Starting with a yellow flame, adding air to the mixture increases the flame speed and also the velocity of flow. Increasing flame speed tends toward flash-back. Increasing mixture velocity tends toward blow-off. With further addition of air stable operation continues with both limits rapidly approaching each other. If the velocity is high enough, no flash-back results, even with the maximum-speed mixture, and the tendency toward flash-back recedes with the decreasing flame speed as the addition of air continues. The increasing velocities of flow, however, soon blow the flame from the port.

If secondary air be excluded, the primary cone alone remains, as in the case of the Smithell's flame separator. The mantle flame around the port rim ordinarily seals the primary cone to the port, but when it is absent it is evident from Fig. 9

that mixtures near maximum flame speed are required to offset the tendency for the velocity of flow to carry the flame off the port.

For maximum usefulness it is obviously desirable to have as large as possible the range of stable operation in respect to rate of flow and composition of the mixture. The effect of the secondary combustion in keeping the flame on the port when the flame speed is low points to the mode of operation of the many "flame-retaining" devices, all of which operate on this principle.

A supplementary port (or ports) around the rim of the burner port is supplied with part of the same mixture at a lower rate of flow, or with a separately controlled mixture of constant composition and velocity, to supplement the mantle flame in maintaining a source of ignition at the port rim. Devices of the former type tested by the writer prevented the blowing off of the flame until the proportion of air in the mixture had reached around 200 per cent of that theoretically required to burn the gas. A device of the latter type will, of course, prevent blowing off entirely, and will burn at least a part of the mixture passing the main burner port even though it be well below the lower inflammable limit.

3. Effect of Temperature of Burner on Stability. With many burners operating properly below 100° or 200°C on a mixture of relatively low flame speed, the flame is blown off the port if the

burner is heated to 300° or 400°C. The flame speed increases with increasing temperature, but the volume of the mixture, and consequently its velocity, are increased so much more than the flame speed that blow-off results. With burners operating properly in a higher range of temperature, or with mixtures of relatively high flame speed in the lower range of temperature (mixtures with oxygen instead of air), the temperature coefficient of the flame speed may be greater than that of the velocity of the mixture, and flash-back may result.

C. Utilization of Heat from Flames

The heat from stationary flames is usually utilized in one of two ways. Either the heat is absorbed and converted at relatively low temperatures, or it is required to raise the body to which heat is being transferred to a high temperature. The flow calorimeter affords an excellent example of the efficient absorption of heat on a large surface kept at a low temperature. An example of the second case is a thermocouple formerly used in attempts to determine the temperature of a flame; the temperature attained by the junction rises until the rate of heat loss from the junction equals the rate at which heat is being supplied to it.

A body receives heat from a flame partly by radiation but mainly by conduction from the hot gases. The rate at which heat is transferred, therefore, is affected by the thermal conductivity of the layer of gases at the surface of the body, and, consequently, depends on the relative proportions of hydrogen, carbon dioxide, water vapor, carbon monoxide, nitrogen, oxygen, and other gases present in the layer in which the transfer takes place. The gases are enumerated in the order in which their effect is of decreasing importance.

If the body is a thermojunction which is small as compared to that part of the flame where the gases are hottest, there is little if any heat carried away from the junction by gases of lower temperature. Heat is lost by conduction through the leads from the junction in relation to their size and temperature, and by radiation from the junction and adjacent leads at a rate depending on their surface area and temperature. Small size of the body to be heated is a prime requisite if its temperature is even to approach that of the gases of the flame.

It is obvious that, in any specific case, the temperature attained by a body of appreciable size in a flame has little or no relation to the "flame temperature" as determined by usual optical methods.

1. *Matching the Flame to the Requirements of the Application.* In selecting a flame for a specific purpose and keeping in mind the points just mentioned, it is usually possible to come to some decision as to the rate at which heat is to be liberated, the fuel gas to be used, the proportion of air or oxygen with which it is to be mixed, the area over which the heat is to be distributed, whether the mixture is to be variable or fixed, and, if fixed, at what composition. Access of secondary air to the flame, the space in which combustion is to take place, and whether transfer of heat by radiation from flame or refractory, or by contact with hot gases alone, is suitable, are important in making some of these decisions. Some of the various compromises involved in the case of domestic gas appliances are discussed in a circular of the Bureau of Standards (C 394, Section VII).

2. *Matching the Burner to the Flame.* There is a somewhat more definite basis for the selection of a suitable burner for a given flame than there is for the selection of the flame for a special purpose. In the interest of stability one would attempt to select a burner with which normal operation is as remote as practicable from both flash-back and blow-off.

Having decided upon the identity of the fuel gas and whether it is to be burned with air or oxygen, the range of variation of composition of the mixture permits the estimation of the range of volumetric rate of flow and the range of flame speeds involved. Values of the latter should, of course, be relative to the mixture, and not taken from the literature indiscriminately.

The relationship between flame speed and average mixture velocity within the limits of stable operation has not been fully investigated as yet. There appears to be no general relation which holds for more than two or three fuel gases in a group, or for burners of different sizes. So far, however, S_M has always been found greater than S_T . With mixtures of city gas and air and a 9.6-mm burner, for example, S_M/S_T = about 3 at flash-back. With mixtures of hydrogen and air and a 3.8-mm burner S_M/S_T = 1.8. At blow-off, with city gas-, carbon monoxide-, and propane-air mixtures and the 9.6-mm burner, S_M/S_T = about 10.

By taking a value for the flame speed and the ratio of S_M/S_T in the mid range (about 6 or 7), an approximate value of S_M can be obtained. From this value and the volumetric rate a tentative diameter for the burner tube may be selected. If a computation of the Reynolds number R (see p. 208), indicates that the flow is turbulent, the stable range between flash-back

and blow-off will be less and the applicable ratios of S_M/S_T will be different.

Studies of the effect of the depth of the port, reported by Eiseman and Smith,⁵ indicate that maximum susceptibility to flash-back occurs when the length (or depth) of the cylindrical port is about one-half the diameter, and that increasing the depth decreases susceptibility to both flash-back and blow-off. Turbulent flow was found to produce a marked increase in susceptibility to flash-back, other conditions remaining constant.

Of course, appropriate modifications in the above computations would be necessary in the case of a burner having multiple ports or other characteristics significantly different from a single smooth cylindrical tube.

3. *Intensity of Combustion.* It has been indicated in Section III-C of this paper that "flame temperature" is not a reliable guide to the relative ability of different fuel gases to heat an object to a high temperature. The maximum flame temperatures of the various gases do not differ very much, but only a few can be used for such operations as welding.

Similarly, the heating value of the fuel gas is no indication of its ability in this respect. For example, the comparison between hydrogen, carbon monoxide, and natural gas shows hydrogen and carbon monoxide to be similar with respect to the heat produced from a cubic foot, and carbon monoxide and natural gas to be about equally poor for use with torches to produce high local temperatures, while the heating value of natural gas is from three to five times that of carbon monoxide or hydrogen. Hydrogen, with the low heating value, is the only one of the three which is suitable for such uses.

Passauer⁹ and Brückner and Jahn² have pointed out that the maximum intensity of combustion should be attained with the maximum-speed mixture, because under these conditions the maximum quantity of heat per second can be liberated in the smallest space. The advantage of this situation in producing high local temperatures is easily seen when one considers that the smaller the area through which the heat escapes, the higher is the temperature gradient required to maintain the flow of heat at a given rate, and, consequently, the higher the temperature attained within the space where the heat is liberated.

Table V compares the combustion intensities of five fuel gases. Heating value and flame temperature are poor criteria by which to compare fuel gases for torch work, because, as heating value increases, so also does the quantity of air or oxygen required for combustion. The heating value of the theoretical mixture of many gases is

TABLE V

Relative combustion intensities of several fuel gases

Fuel gas	Net heating value, Btu/cu ft	Heating value of maximum S_T mixture, Btu/cu ft	Maximum flame speed, ft/sec	Combustion intensity, Btu/sec/sq ft
CH ₄	895	89	1.1	98
C ₂ H ₆	1607	95	1.4	133
C ₂ H ₄	1473	106	2.5	265
C ₂ H ₂	1414	135	4.7	634
CO	315	143	1.4	200
H ₂	269	117	8.8	1030

not far from 100 Btu per cubic foot. The maximum-speed mixture differs from the theoretical by varying amounts for the different gases, and the heating value of the former is slightly the higher. The mixture with which maximum flame temperature is attained is not far from the maximum-speed mixture. The heating value for these mixtures is of the same order of magnitude for all the gases, thus accounting for the similarity of the "flame temperatures."

The maximum flame speed is thus left as the significant and controlling factor in determining the intensity of combustion. The means by which intensity can be controlled are those which affect flame speed. The substitution of premixed primary air for diffusion processes with secondary air, of ethylene, acetylene, or hydrogen for carbon monoxide or the paraffin hydrocarbons, of oxygen for air in the mixture, and preheating the mixture, all increase flame speed and intensity of combustion.

D. Turbulence, Flame Speed, and Noise

Scattered through the literature are numerous statements, often conflicting, concerning the interrelationships between turbulent flow, flame speed, and noise. It seems very improbable that turbulence would have any effect on the speed of the flame relative to the mixture, but it does increase the mass rate of burning by increasing the area of the flame surface.

Probably the most exhaustive and careful study of these problems has been Project No. 13 of the Committee on Industrial Gas Research of the American Gas Association.¹ This work shows without question that, in general, noise increases with the velocity of flow of the mixture and with the flame speed, and that no noise

results when a homogeneous mixture emerges from the ports in laminar flow. (In the latter case the flame front is at rest.)

Of course, in excess of the critical velocity, turbulence increases as the velocity of the mixture increases. Thus, increasing noise may result from a simultaneous increase in turbulence and in flame speed, which might then be associated by the unwary as cause and effect. It is more probable that the flame speed is fixed by the properties of the mixture, regardless of the vagaries of motion of the medium in which the flame travels.

There is little doubt that the source of the sound is in the random disorganized changes of position of the flame front. The part of the flame which is most active depends on individual circumstances. It may be the flickering at the base, caused by intermittent blow-off, which can be remedied by the use of any means which keeps the flame seated on the port. It may be the entire flame surface in a jumble of random incipient flash-back and blow-off, in a multiplicity of explosions of small masses of mixture partially detached from the stream and ignited separately.

In some cases, like those reported by Eiseman and Smith,⁵ there might be some reason to suspect that the noise was the result of resonance in the burner. The sound, at times, approached a pure note, the pitch and loudness of which increased with flame speed and rate of flow. The flame surfaces could be observed in rapid alternation between two sharply defined positions. The sound was absent, however, when the mixture, otherwise unchanged in any way, was allowed to flow without ignition.

IV. Summary and Conclusions

Numerical values for flame speeds obtained with burners are affected by the various ways in which the measurements of the flames are made, by experimental conditions, and by the different ways in which the results are computed.

Measurements of the angle between flame surface and axis at a point $0.7r$ from the axis, on flames resulting from mixtures in laminar flow at or near the composition for maximum flame speed and on burners over 4 mm in diameter, yield results affected by variations in experimental conditions.

Maximum flame speeds alone are suitable for making comparisons between different fuel gases because of the lack of any common basis (in point of composition) for comparison.

An appreciable redistribution of velocities in the stream of the mixture takes place as the stream leaves the port. This takes the form of an

acceleration near the boundaries of the stream and a deceleration near the axis, and affects the shape of the flame surface.

Although burner methods of measuring flame speed are relatively simple and the results directly applicable to a multitude of burner problems, the field of usefulness of the method appears at present to be considerably restricted by the limitations mentioned above.

The usefulness of flames is dependent on their stability and susceptibility to control. Laminar flow, favored by deep ports and small diameters of the port, increases the range of stable operation between the limits of flash-back and blow-off. Complete mixing and low proportions of air do likewise. Such conditions also tend to eliminate turbulence and noise.

In the absence of secondary air, the maximum range of stable operation is found with the maximum-speed mixture. The range is about half that in secondary air, and decreases rapidly as the composition of the mixture is changed in either direction.

In selecting a flame for a definite purpose one should keep in mind the fact that the temperature attained by the body being heated rises until the rate at which heat is lost becomes equal to the rate at which it is supplied.

In choosing the dimensions of a burner for a given flame, a likely value for the average velocity of flow of maximum-speed mixtures with air will be from six to seven times the maximum flame speed.

Where local high temperatures are required, they can be obtained by providing conditions which result in the liberation of heat at the highest rate in a given space. Maximum flame speed rather than flame temperature or heating value of the gas is the key to this. The heating value of the maximum-speed mixture, multiplied by the maximum flame speed, is an index to intensity of combustion (Btu per second per unit area).

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COMPARISON OF IDEAL AND ACTUAL COMBUSTION TEMPERATURES AND PRESSURES: ANOMALOUS EFFECTS; GAS VIBRATIONS*

GUENTHER VON ELBE

Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pennsylvania

AND

BERNARD LEWIS

Explosives Division, Pittsburgh Experiment Station, U.S. Bureau of Mines, Pittsburgh, Pennsylvania

The calculation of flame temperatures, expansion ratios of flames, and explosion pressures for the case of ideal, i.e., complete and adiabatic, combustion, involves the solution of a number of equations, which may be divided into three groups. One equation represents the energy balance of the system; that is, the energy released in the chemical reaction equals the thermal energy gained by the system. The second group comprises several equations describing the material balance of the system, one equation for each atomic species participating in the reaction. The third group comprises the dissociation constants of the chemical equilibria involved. The solution of the equations is a somewhat involved procedure, but it presents no fundamental difficulties. The calculations can be made accurately by the use of energy contents and equilibrium data determined from band spectroscopy.⁷

In explosions in closed vessels with local ignition one must also take into consideration the effect of the temperature gradient in the vessel at the end of the explosion on the pressure developed. This has been discussed elsewhere, and it has been shown that the temperature gradient lowers the pressure a few tenths of a per cent, depending on the mixture composition.⁸

To approach as closely as possible to adiabatic combustion the flame gases should not be in contact with cooling surfaces. In closed-vessel explosions this condition is most nearly realized in spherical vessels with central ignition. The flame is insulated from the wall by a layer of unburnt gas up to the point of maximum pressure. It is, however, unavoidably in contact with the ignition rod. One may minimize heat loss by making the latter as small in diameter as possible and choosing a reasonably large vessel, avoiding, as far as possible, deviations from the spherical contour of the vessel. Radiation loss could be reduced by polishing the wall, but it appears that possibly only in slow carbon monoxide explosions

is the thermal radiation of carbon dioxide not negligible.

Table I contains a summary of comparisons between ideal and experimental explosion pressures for hydrogen-oxygen explosions.⁹ The explosion pressures were observed by a number of investigators—Pier, Bjerrum, Wohl and Magat, and Lewis and von Elbe.

In Explosions (a) excellent agreement is obtained between experimental and calculated pressures, indicating that within the limits of accuracy of measurement these explosions are ideal. The slightly low results in Explosions (b) have been shown to be due to heat loss to the ignition rod, the gas containing a large excess of hydrogen and therefore being highly conductive.

Explosions (c) illustrate the results with dry hydrogen-oxygen mixtures. The observed pressures are, on the average, 2 per cent below the calculated, a discrepancy that lies outside the experimental error. When small amounts of water vapor are added to the initial mixture the discrepancy disappears except for the heat loss through the ignition rod, 1.3 mm of water vapor being sufficient to do this. Furthermore, as shown by other experiments not included in the table, the deviations from the ideal explosion pressures decrease as the initial pressure is increased to several atmospheres. The following explanation has been proposed for the phenomenon. The discrepancy is due to loss of energy by luminescent radiation from the flame front. Highly vibrating molecules of OH or H₂O are formed in the reaction, which radiate unless quenching takes place by a collision of the second kind with appropriate molecules such as diluent unexcited H₂O. The luminescence radiation may also be quenched by increased pressure. To date, experimental confirmation of this explanation is still lacking.

In Explosions (d) the observed pressures are higher than the calculated, the anomalous effect being greater in excess oxygen than in nitrogen mixtures. The effect disappears when the oxygen or nitrogen is replaced by helium or argon. The anomaly can be reasonably explained only by assuming that there is a momentary excess of

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TABLE I

Average percentage deviation of observed from calculated explosion pressures for hydrogen-oxygen mixtures containing different inert gases

Type of mixture	Number of explosions	Average percentage deviation of observed from calculated pressures
(a) $(\text{H}_2, \text{O}_2) + \text{small excess of H}_2 + \text{A} + \text{H}_2\text{O}$	15	+0.07
(b) $(\text{H}_2, \text{O}_2) + \text{large excess of H}_2 + \text{H}_2\text{O}$	11	-0.61
(c) $(\text{H}_2, \text{O}_2) + \text{large excess of H}_2; \text{dried with P}_2\text{O}_5$	10	-2.00
(d) $(\text{H}_2, \text{O}_2) + \text{excess O}_2 + \text{H}_2\text{O}$	6	+1.22
$(\text{H}_2, \text{O}_2) + \text{N}_2 + \text{H}_2\text{O}$	8	+0.79

translational energy at the end of the explosion. This could be the case if a time lag exists in the excitation of the vibrational energy levels in oxygen and nitrogen molecules. The energy released in the chemical reaction then flows first into those degrees of freedom that offer least hindrance. These are particularly translation and also rotation. The explanation is supported by experiments on the velocity of sound in these as well as other gases, notably carbon dioxide, carbon monoxide, nitrous oxide, and chlorine, where the existence of such an excitation lag was established.

It is noteworthy that excitation lag is not observed in explosions of ozone diluted with oxygen.⁹ This would indicate that the highly energized molecules of oxygen emerging from elementary reactions of decomposing ozone are capable of distributing their excess energy among all degrees of freedom of diluent oxygen molecules—namely, molecules of their own kind—in an extremely short period of time compared with the progress of the flame front. The process by which this energy distribution takes place may be discussed briefly. It may be assumed that vibrational quanta are readily transferred in collisions between two oxygen molecules. If the transfer takes place between two neighboring quantum states, there is perfect resonance and no interchange of translational or rotational energy with vibrational energy will occur. If, however, the transfer occurs between more remote quantum states, then, owing to the smaller energy quantum of the upper level, other forms of energy, translational and rotational, must participate in the transfer. Thus in sound velocity experiments⁵ which have been carried out near room temperature and where only the first vibrational level is excited, the vibrational

quantum has a long lifetime and no interchange with other forms of energy occurs. In ozone explosions the oxygen molecules are excited to various high vibrational levels, and the exchange of vibrational energy leads to interchange with other forms of energy and thus to rapid establishment of thermodynamic equilibrium.

It is of interest that ozone explosions yield a value of the electronic $^1\Delta$ level of the oxygen molecule of 0.85 ± 0.1 volt,¹⁰ compared with the spectroscopic value of 0.97 volt.⁴ The closeness of the agreement is emphasized by the fact that at the highest explosion temperature, 2500°K , the difference between the observed and spectroscopic values amounts to less than 10° difference between the observed and theoretical explosion temperature and is in the direction to be accounted for by slight heat loss during the explosion.

For carbon monoxide-oxygen explosions experiments of Pier¹² and David and Leah² are available. They have been compared with ideal pressures by the present authors.* Pier exploded dry and moist mixtures; David and Leah exploded mixtures containing a small percentage of hydrogen. In Pier's experiments the pressures fall generally several per cent below the calculated except for a mixture containing a large excess of carbon monoxide, where the reverse is true. Here the heat loss is presumably overshadowed by excitation lag. David and Leah's experiments show generally much smaller pressure loss. In mixtures containing a large excess of carbon monoxide the observed pressure is again larger than the calculated. That heat losses in carbon monoxide-oxygen explosions considerably

* For details consult Lewis and von Elbe: *Combustion, Flames and Explosions of Gases*, Cambridge University Press, 1938.

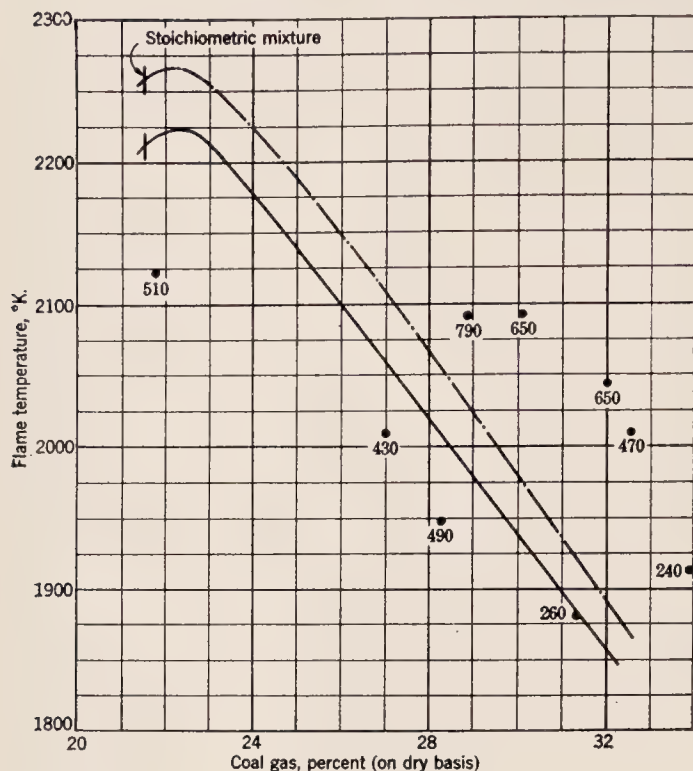


FIG. 1. Comparison of theoretical flame temperatures of coal gas-air mixtures with experimental flame temperatures determined by the line-reversal method. — · —, theoretical curve, dry mixtures; —, theoretical curve, moist mixtures; ●, sodium line-reversal flame temperatures with gas velocity in centimeters per second.

exceed those in hydrogen-oxygen explosions is not surprising in view of the much longer duration of the former explosions (of the order of tenfold), which accentuates radiation loss and conduction to the ignition rod and causes early contact of the burnt gas with the wall, owing to convective rise. Concerning the differences in heat losses in Pier's and in David and Leah's experiments, it is probable that the presence of a small amount of hydrogen in carbon monoxide-oxygen mixtures shortens the combustion time more than the presence of water vapor.

Pier's¹² explosions of mixtures of acetylene and oxygen show that excitation lag is more pronounced with oxygen as diluent than with nitrogen. This agrees with the experience in the hydrogen-oxygen explosion series. Diluent carbon dioxide also shows a strong excitation lag.*

Expansion ratios have been measured by soap-bubble explosions of mixtures of carbon monoxide and oxygen diluted or not with helium or argon.³ The results show a trend similar to that found for the explosion pressures in spherical vessels. On the lean side the expansion ratios fall below the calculated considerably more than in the case of explosion pressures. Apart from radiation loss one must again consider the cooling effect of the ignition rod. The latter consisted of metal wires. Since the mass of gas used in these soap-bubble

explosions was much smaller than in Pier's and in David and Leah's spherical-vessel explosions (of the order of $\frac{1}{100}$), a considerably greater percentage heat loss through the ignition rod is to be expected. On the rich side the expansion ratios are grouped more closely around the calculated values. It is suggested that here there is a partial cancellation of heat loss by excitation lag.*

There does not seem to be any way to reconcile the very low flame temperatures measured by David¹ with a platinum-wire thermometer in the early stages of flame in a spherical vessel, with the above results. One may suspect errors in the temperature measurements. David and Leah's results discussed above are also in disagreement with these wire temperature measurements.

The sodium line-reversal method, the reliability of which has been proved by the work of Kohn⁶ and others, is particularly suited for measurement of the temperature of stationary flames. Consideration of the structure of stationary flames such as Bunsen or Méker flames, points to an uncontrollable admixture of the surrounding atmosphere, particularly at the base of the cone. Therefore measurements of the temperature of such flames should be interpreted with caution. If the temperature is measured solely in some interior portion of the flame, then the protection afforded by the outer flame should suffice to bring such measurements into substantial agreement with the experience on explosion pressures and expansion ratios. This is the case. It is,

* For details consult Lewis and von Elbe: *Combustion, Flames and Explosions of Gases*, Cambridge University Press, 1938.

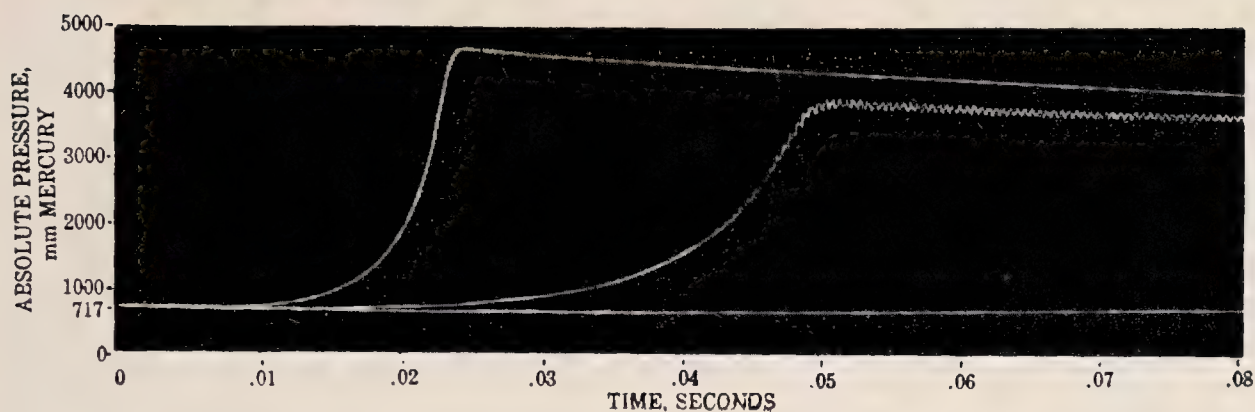


FIG. 2. Vibration effect in hydrogen-air explosions. Slower explosion, 15 per cent of hydrogen; faster explosion, 20 per cent of hydrogen.

however, to be borne in mind that heat losses occur to the grid of the Méker burner. These losses can be reduced by increasing the gas velocity.

Figure 1 shows some results obtained by Minkowski, Müller, and Weber-Schäfer¹¹ with rich coal gas-air mixtures containing an unspecified amount of water, using the line-reversal method and a protected flame. The curves are flame temperatures calculated by the present authors for dry and for water-saturated mixtures. It is noted that the experimental points fall below as well as above the theoretical curve, and that they arrange themselves according to the gas velocity. The closer the mixture is to the stoichiometric, the larger the gas velocity required to raise the temperature of a given mixture to or above the theoretical curve. This can be explained by the higher flame speed of such mixtures, which brings the burning gas closer to the grid, thus increasing the grid loss. Some values fall considerably above the theoretical curve, again pointing to excitation lag.

The results with Pittsburgh natural gas described by Kaveler and Lewis in the next paper are in harmony with the above results. Since the flame speed of natural gas is much smaller than that of coal gas, both grid losses and excitation lag are less pronounced, the latter because there is much more time for the establishment of thermodynamic equilibrium.

The excitation lag seems to be responsible for the occurrence of the peculiar gas vibrations that appear in closed-vessel explosions and that have been observed by many investigators⁹ with various explosive mixtures between certain limits of composition in vessels of various shapes and sizes. Figure 2 shows the effect in hydrogen-oxygen mixtures diluted with nitrogen. It is observed that the vibrations commence long before maximum pressure, beginning when the

pressure starts to rise steeply, and that they occur only in the slower of the two explosions. With an equal amount of oxygen as diluent, the vibrations are so intense that it is impossible to obtain a pressure record. The vibrations do not appear in mixtures containing excess hydrogen, helium, or argon. There seems to be little doubt, therefore, that they are in some way connected with the ability of the gas mixture to exhibit the excitation lag. The origin of the vibrations may be proposed as follows: Normally one expects the excitation lag to be localized in the freshly burnt gas forming a shell around the burnt core, since considerable time has elapsed since the core burned. The persistence of the excitation lag is an inverse function of the temperature, probably of an exponential character. Therefore in low-temperature explosions the chances are better that the lag persists in the deeper layers of the core. When the rate of pressure rise becomes steep, there is a steep rise in the temperature of the core, causing a rapid increase in the rate of attainment of energy equilibrium and consequently a rapid shrinkage in volume of the inner layers of gas. This results in a sudden inward mass movement of the gas which may be likened to an implosion. In this way pressure waves are set up which, because of little damping, continue for some time. The disappearance of the phenomenon on enriching the mixture may be ascribed to the higher combustion temperature which shortens the duration of the excitation lag in the inner gas layers.

Summary

In moist hydrogen-oxygen mixtures diluted with argon, helium, or excess hydrogen, explosion pressures are found that agree with the theoretical pressures calculated from band spectroscopic data. In dry mixtures the observed

pressures are lower, possibly owing to heat loss by luminescence radiation. In moist mixtures diluted with nitrogen or excess oxygen the pressures are higher. This has been ascribed to the time-dependence of specific heats, called excitation lag. This excitation lag has been linked to gas vibrations which appear early in the explosion. The results with carbon monoxide-oxygen and with acetylene-oxygen mixtures can also be interpreted by heat loss and excitation lag. If a small amount of hydrogen is added to carbon monoxide-oxygen mixtures the heat loss appears to be reduced considerably, probably owing to the shorter duration of the explosion. Excellent agreement is found between experimental and theoretical explosion pressures in ozone-oxygen mixtures. An explanation of the absence of excitation lag in the latter is proposed. Measurements of expansion ratios in soap-bubble explosions of carbon monoxide-oxygen mixtures and flame temperatures by the line-reversal method of coal gas-air mixtures show a trend similar to explosion pressures in hydrogen-oxygen and carbon monoxide-oxygen mixtures.

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FLAME TEMPERATURES AND VERTICAL GRADIENTS IN NATURAL-GAS FLAMES*

H. H. KAVELER AND BERNARD LEWIS

Explosives Division, Pittsburgh Experiment Station, U.S. Bureau of Mines, Pittsburgh, Pennsylvania

The purpose of the experiments described in this paper was to obtain information on the state of the burnt gas that emerges from a flame by comparing observed maximum flame temperatures determined by the sodium line-reversal method with calculated theoretical temperatures, and by investigating very carefully the nature of the temperature gradients in the vertical direction above the cones of suitably constructed stationary flames.

Experimental Method and Procedure

The accuracy and reliability of the line-reversal method for measuring flame temperatures have been demonstrated by a number of investigators² and the method has become standardized. The apparatus used was essentially that employed in previous experiments in this laboratory.¹ Some modifications in the details of the apparatus and procedure will be described here.

Two-stage reducing valves with surge chambers of appropriate size were employed to give a steady flow of the gases so that a very steady flame was produced. Air and/or oxygen was passed first through a sodium chloride-vaporizing chamber before entering a mixing chamber. The mixing chamber was a 500-cc flask in which the natural gas and air or oxygen were premixed before entering the burner.

The composition of the combustible entering the burner was determined from two samples (250 cc each) which were slowly withdrawn from the mixing chamber. A measurement of temperature gradient usually required thirty minutes, so that one sample was withdrawn during the first ten minutes and the other during the last ten minutes of this period. The gas was analyzed with a conventional Orsat apparatus. The per cent of oxygen was determined by absorption with pyrogallol reagent up to a concentration of 30 per cent and with chromous acetate reagent when the concentration exceeded this value. Pittsburgh natural gas in the combustible mixture was determined by combustion over a heated platinum wire, the content being determined from the sum of the contraction and carbon dioxide, using a factor determined by careful Orsat analyses of the natural gas. The accuracy of the analyses is 3 per cent or better, as deter-

mined by duplicate analyses on each sample taken.

The tungsten-band lamp used in these experiments was aged and calibrated by the manufacturer. The calibration was frequently checked during the course of the work and was found to be constant. The current through the lamp was read to 0.10 ampere, equivalent to $\pm 5^{\circ}\text{C}$. The reversals could be easily read to that limit even for natural gas-oxygen flames for which the reversals become more difficult to follow, owing to the low intensity of the D-radiation from these flames. This is probably due to the suppression of the sodium-atom concentration by the presence of the large excess of oxygen in the gases.

A color correction ($+26^{\circ}\text{C}$) and a lens correction (-20°C), as explained elsewhere,¹ were applied to the observed temperatures.

An Important Experimental Requirement

Stationary flames have both vertical and horizontal temperature gradients. The horizontal gradients arise mainly from the interdiffusion of air from the surrounding atmosphere, which causes either secondary combustion or dilution depending upon whether a rich or a lean mixture is being burned. The temperature of the sodium layer nearest the spectroscope determines, for the most part, the temperature reading. In totally colored flames this sodium layer is greatly affected by such interdiffusion. It was desired to eliminate as far as possible this complicating effect of the horizontal temperature gradient. This could easily be accomplished by coloring only the central part of the flame, so that the temperature observations were confined to presumably isothermal horizontal sections protected from secondary air.

Type of Burner

In order to obtain centrally colored flames a concentric-tube burner was used. The details of the construction of this burner are shown in Fig. 1. The outer brass tube of the burner was threaded (40 threads per inch), so that by means of the graduated knurled nut the burner could be moved in the vertical direction.

A number of attempts were made to produce a partially colored single-cone flame over the concentric-tube burner, but the single cone was

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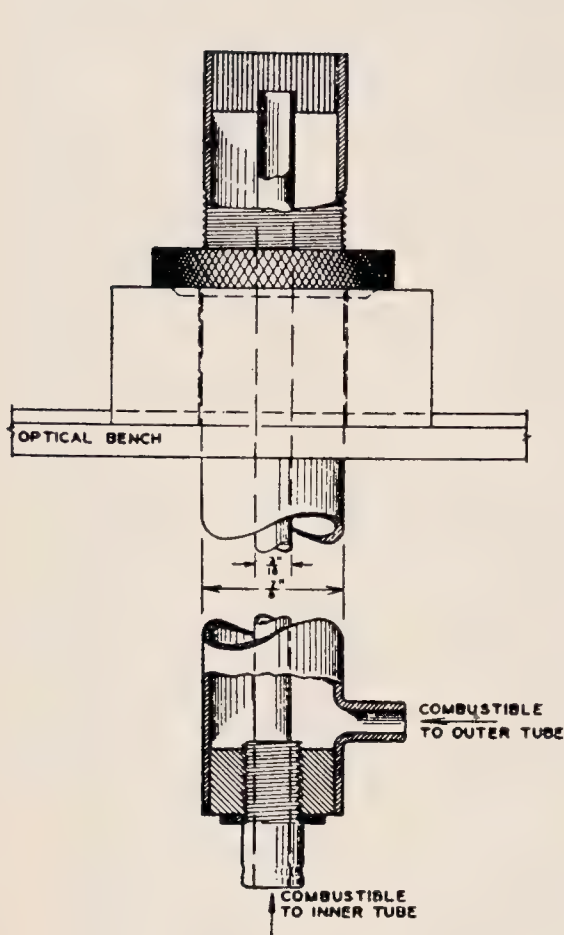


FIG. 1. Concentric-tube burner for producing partially colored flames.

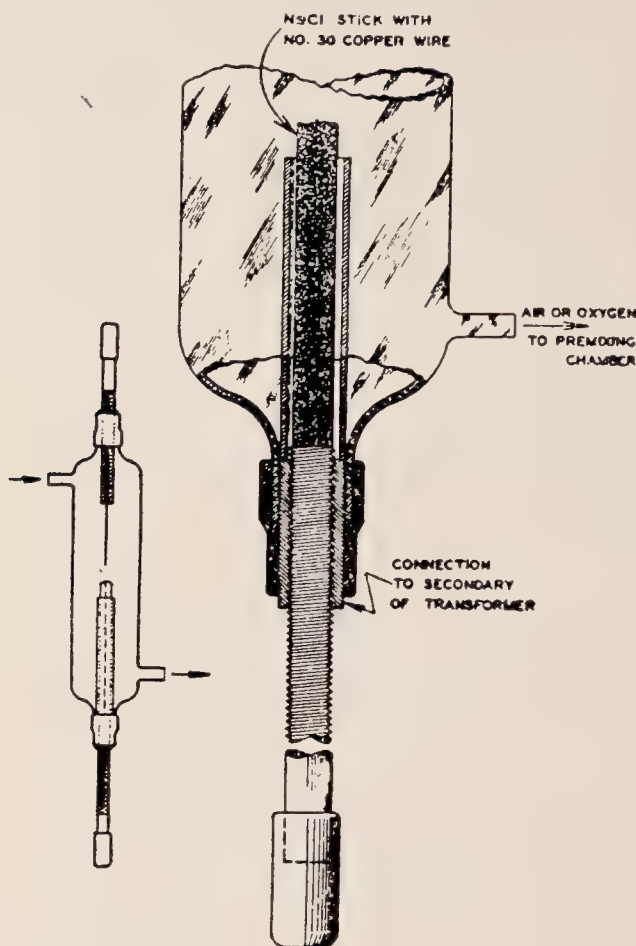


FIG. 2. Detail of sodium chloride electrode and vaporizer.

unstable and vibrated excessively, with a tendency to form a double flame consisting of a cone system on each tube. Temperature observations on partially colored flames were finally made using a nichrome grid. The grid was made from strips of metal 0.5 mm thick forming a square mesh 2 mm on edge over the cross section of the burner.

Method of Introducing Sodium

The conventional wet method of coloring flames causes water droplets to be introduced into the combustible mixture. In order to eliminate any uncertain effects from this source, we used the following electric-arc method of introducing sodium into the combustible mixtures: A sodium chloride vaporizer, represented in Fig. 2, was made from a glass tube drawn down to fit brass bushings which were $\frac{3}{8}$ in. by 1 in. and were fastened to the glass by rubber tubing. The electrodes for producing the electric arc were a No. 18 platinum wire and a stick of sodium chloride attached to bolts as shown in the figure. The stick of sodium chloride was $\frac{1}{4}$ in. by 6

in. and was prepared by compressing moistened salt at a pressure of three or four thousand pounds per square inch in a special mold made from two machined steel blocks. The sticks were air-dried for ten days, after which they could be handled without breaking easily. A radial groove was cut down the length of each stick so that a length of No. 30 copper wire could be placed down the center of it. The copper-wire core is an essential feature of the sodium chloride electrode, for it keeps the arc directed to the center of the salt stick, whereas otherwise it would tend to follow a path in the ionized air. The sodium chloride stick was glued to the lower bolt to which one end of the copper wire was soldered. A brass-tube guide was used to keep the salt stick centered in the glass tube. A 250-watt transformer delivering 2000 volts on the secondary was used to supply energy for vaporizing the salt stick. Lower voltages were not so satisfactory for maintaining a continuous arc for long periods. It is essential that the size of the copper wire be so chosen that it will burn away at the same rate as the salt stick. The vaporizing device was operated manually. After the arc was struck, the sodium

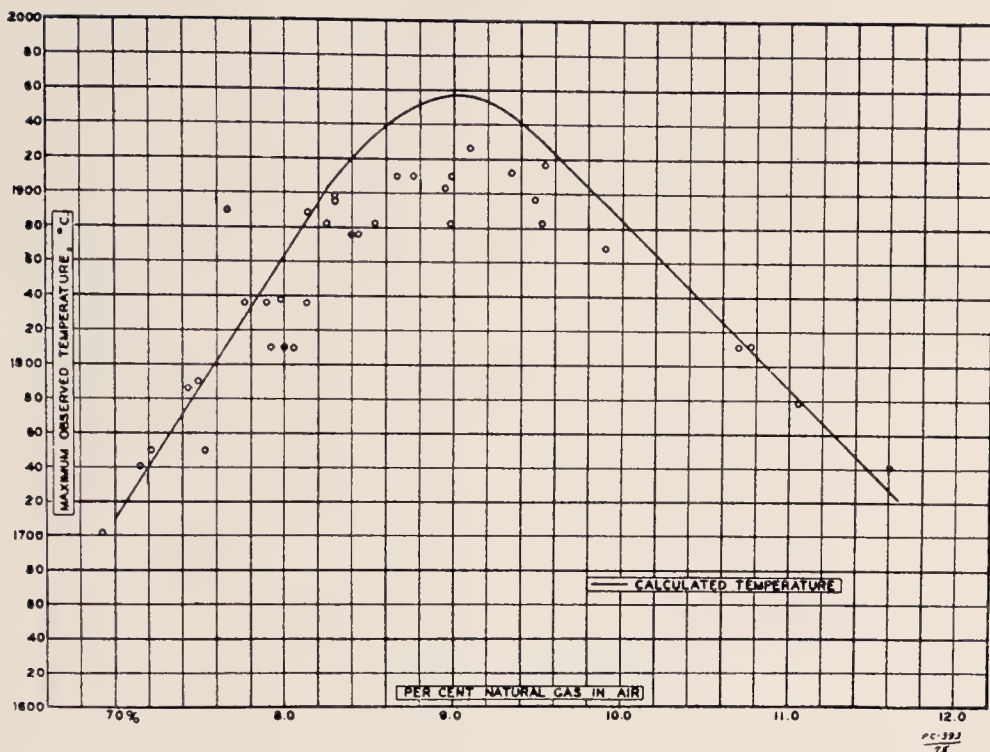


FIG. 3. Maximum observed temperatures; partially colored natural gas-air flames.

chloride was fed into the system by screwing in the lower bolt. At each setting, the stick would burn for three or four minutes, which was sufficient time for a temperature reading. The amount of salt vaporized in the stream could be easily regulated and maintained constant by varying the energy input of the transformer.

Oxygen or air was passed through the vaporizer from which the salt-laden gas passed to the mixing chamber. At the mixing chamber the gas was divided into two streams. One passed directly to the inner tube of the burner, and the other to the outer tube through a filter to remove sodium chloride dust. The filter consisted of a wad of cotton, 6 in. thick, flanged into a can 12 in. in diameter and 8 in. deep. The pressure drop through this filter was very small, and the flow through either channel was regulated by pinch clamps on the line. The procedure of premixing the gas and removing a portion of the salt vapor was necessary to insure uniformity of combustible composition in both streams.

Composition of Pittsburgh Natural Gas

The natural gas used in the experiments was taken from the laboratory supply and compressed to 1500 lb. in a large cylinder.

The average of six Orsat analyses of this gas was as follows: methane; 85.48 per cent; ethane, 13.85 per cent; nitrogen, 0.67 per cent. The maximum deviation from this average was 0.40 per cent. A sample of the gas was also subjected

to a low-temperature fractionation, and the result was: methane, 88.6 per cent; ethane, 9.3 per cent; propane, 1.8 per cent; butane, 0.3 per cent; nitrogen, nil. Considering 0.67 per cent nitrogen (undetectable) as present in the methane fraction, this analysis is in satisfactory agreement with the Orsat analysis.

Calculated Flame Temperatures

The theoretical flame temperatures for Pittsburgh natural gas with air and with oxygen were

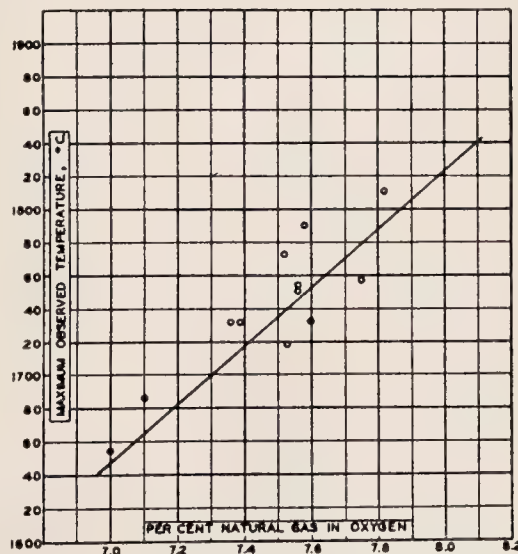


FIG. 4. Maximum observed temperatures; partially colored natural gas-oxygen flames

TABLE I
Flame temperatures of completely and partially colored flames*

Height above cone, mm	Temperature, °C		
	A	B	C
-0.6	1654	1638	
0.0	1678	1694	1741
+0.6	1686	1710	1778
1.9	1710	1764	1810
3.2	1718	1790	1852
4.4			1882
6.4	1686	1824	1896
9.5	1615	1838	1896
12.7		1838	1896
15.9		1838	

A: completely colored flame over $\frac{3}{8}$ -in. grid; B: completely colored flame over $\frac{7}{8}$ -in. grid; C: partially colored flame over $\frac{7}{8}$ -in. grid.

* 8.52 per cent natural gas in air.

calculated by the method outlined by Lewis and von Elbe,³ and are given by the curves in Fig. 3 and 4. The heats of combustion used were those given by Rossini.⁵ The heat capacities and dissociation equilibria used for the temperature calculation were those compiled by Lewis and von Elbe⁴ from spectroscopic data. The calculated temperature is but slightly changed if one expresses the composition of natural gas as methane and ethane rather than in terms of its true hydrocarbon content. This is the case since the respective heats of combustion are nearly the same per mole of water and carbon dioxide formed, and because the bulk of the gas is methane. The values are correct to within 2° to 4°C.

Observed Temperature Gradients in Flames of Natural Gas and Air

Some preliminary temperature observations were made on completely colored flames using a $\frac{3}{8}$ -in. brass tube with a grid as the burner. The observed maximum flame temperatures agreed quite well with those previously reported from this laboratory.¹ As usual with completely colored flames, the observed temperatures were higher than the calculated on the rich side and lower on the lean side. There was always a positive temperature gradient above the tips of the cones, with the maximum temperature about 5 to 6 mm above the cones. When the nitrogen in the air was replaced by oxygen, the point of maximum temperature approached the cones, and at about 50 per cent oxygen there was no vertical gradient for 1 to 2 cm above the cones.

The effect of coloring just the central portion of the flame is shown in Table I. The temperature of the partially colored flame is considerably higher than that of a completely colored flame of the same size. The data given for the small, completely colored flame indicate that the effect of secondary air becomes greater as the flame size is reduced. The effect of partially coloring flames for line-reversal temperature measurements, as shown in Table I (column C), is typical of the experiments reported in this paper.

As the space velocity of the combustible mixture is increased, the gradient above the cones shifts to a higher temperature range and becomes smaller, while the maximum temperature is maintained over a greater distance. This is shown in Table II.

The positive gradient above the cones of these natural gas-air flames may be explained as arising from heat losses through the grid. Relatively cold layers of gas rise in the centrally

TABLE II
Effect of space velocity on temperature gradient and maximum temperature*

Height above cone, mm	°C for cubic feet per second through burner				
	0.00060	0.00094	0.00119	0.00159	0.00201
-1.3	1654				
-0.6	1686				
0.0	1702	1718	1726	1732	1750
+0.6	1718	1718	1832	1750	1764
3.2	1732	1732	1750	1764	1778
5.4	1718	1750	1764	1778	1778
9.5	1702	1741	1750	1778	1772
12.7				1778	1764

* 10.85 per cent natural gas in air.

colored stream from the base of the cones near the grid enveloping the colored stream, and give rise to an observed temperature lower than the average temperature over the cross section. Due to mixing above the cones these cold layers disappear, and the observed temperature increases. When the space velocity is increased the grid losses are decreased (Table II).

In Fig. 3 the maximum observed flame temperatures for various mixtures of natural gas and air are compared with calculated theoretical flame temperatures. For lean and rich mixtures the agreement between observed and theoretical temperatures is very close. In the region of the maximum temperature, the observed temperatures are 20° to 40°C below the theoretical. Table III permits a comparison of the temperature at the cones and the maximum observed temperature for experiments recorded in Fig. 3. The temperature differences are, on the whole, smaller for the leaner mixtures. This is further evidence that heat losses are smaller for lean mixtures, as may be expected from the lower temperatures of the flames and from the greater separation of the burning zone from the grid owing to lower flame speeds.

The scattering of the experimental points in Fig. 3 is mainly due to the difficulty of maintaining the mixture composition constant.

Experiments with Natural Gas-Oxygen Mixtures

The maximum flame temperatures for these flames were observed immediately at the cone. Above the cone the flame temperature decreased uniformly for several centimeters from this point. Since the flame speed in oxygen mixtures is faster than in air mixtures, the space velocity in these experiments was much greater. The experimental maximum temperatures are compared with the theoretical calculated temperatures in Fig. 4, where it is seen that the experimental points tend to be higher than the calculated. In view of the fact that heat losses occur, the negative gradient above these flames indicates the existence of excitation lag (see preceding paper). The latter would obscure the positive gradient arising from heat losses, since these are smaller in oxygen flames owing to the high space velocity.

Summary

Flame temperatures were measured by the sodium line-reversal method along the vertical axis of centrally (partially) colored Méker flames for mixtures of natural gas with air and oxygen. For air mixtures the vertical temperature gradient above the cones is positive. The tempera-

TABLE III

Difference between temperature above the cones and maximum temperature for natural gas-air flames

Natural gas in air, %	Flame temperatures, °C		Distance above cone, mm	Temperature difference, °C
	At cone	Max.		
6.51	1568	1638	3	70
7.15	1650	1741	5	91
7.22	1690	1750	9	60
7.44	1742	1786	9	44
7.54	1670	1750	9	80
7.67	1786	1890	8	104
7.77	1746	1836	9	90
7.90	1746	1836	9	90
8.00	1742	1810	9	68
8.06	1766	1810	9	44
8.13	1718	1836		118
8.14	1738	1888	10	150
8.31	1778	1898	8	120
8.53	1734	1882	6	148
8.99	1776	1910	8	134
9.35	1810	1912	9	102
9.48	1766	1896	9	130
9.55	1810	1916	9	106

ture range and length of the positive gradient depend upon space velocity and mixture composition. In oxygen mixtures the maximum temperature is found immediately above the cones, and the vertical gradient is a uniform negative gradient for several centimeters.

The maximum observed temperatures in air mixtures show the greatest deviation from the theoretical near the stoichiometric point, being about 20° to 40°C lower. The maximum temperatures of oxygen mixtures on the average slightly exceed the theoretical. The results are explained on the basis of heat losses, particularly to the grid, and the excitation lag in oxygen mixtures.

Acknowledgment

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FLAME TEMPERATURES IN ENGINES

A. E. HERSHEY

Department of Mechanical Engineering, University of Illinois, Urbana, Illinois

Thermodynamic analysis of the transformation of chemical energy into mechanical energy in an internal-combustion engine may be carried out in two different ways. In the first and simplest method of analysis, the energy equation is applied directly to the process, without considering any of the various separate transformations; the engine then becomes a concealed mechanism and its performance is determined by the measurement of external effects. These external effects consist of a flow of gas into and out of the engine, and the transfer of energy in the form of heat and mechanical work to the surroundings. Energy is also transported into and out of the engine along with the gas stream. For this process the energy equation becomes

$$M_2h_2 - M_1h_1 = {}_1Q_2 - {}_1W_2,$$

where M_1 and M_2 are, respectively, the number of moles of gas entering and leaving the engine, h is the enthalpy per mole of mixture, ${}_1Q_2$ is the heat transferred, and ${}_1W_2$ is the work done. The state of the entering mixture and hence the term M_1h_1 are usually known, and when any two of the remaining terms can be determined independently, the third term can be readily found from this equation. Such an analysis, while completely rigorous, gives rather trivial information about the performance of an engine, and therefore is of little practical value in considering ways and means of improving this performance.

The second method of procedure is to consider separately each of the energy transformations which occur in the engine and then determine engine performance from the net effect of all these transformations. Such a procedure has the advantage of supplying detailed information about the separate transformations, but does so at the expense of difficult and involved analysis. Thus, while the induction, mixing, and compression of the fresh charge presents little or no difficulty, the transformations during combustion and the early portion of expansion can be treated analytically only after the introduction of a number of simplifying assumptions. In addition, detailed information is required concerning the thermal, chemical, and physical properties of the gases which constitute the working medium. The ultimate test of the validity of these assumptions and the accuracy of these data is the precision with which the state of the gases can be determined at certain points throughout the cycle.

The method of analysis which has just been briefly outlined has been used in the study of

ideal, or theoretical, cycles^{5,2,12,9} and also in analyzing experimental data from actual engine tests.¹⁹ However, before making extensive use of the method, it is very desirable to apply some such test as that just mentioned, in order to form an idea of its reliability and precision. The crucial portion of any internal-combustion engine cycle is that during which chemical energy is being transformed into thermal energy by combustion and thence into mechanical energy by expansion of the heated gas; it is needless to add that this is also the most difficult to analyze. The present discussion is chiefly concerned with the determination of the state of the working medium during combustion and the early part of expansion in an engine operating on the Otto cycle.

Gases in an Engine Considered as a Thermodynamic System

In order to apply thermodynamics to the energy transformations which occur during combustion and expansion in the cylinder of an engine, it is necessary to define exactly the system and the changes of state which are to be considered. The system consists of a mixture of gases, whose state at any instant is completely determined when suitable values can be assigned to the following variables: the total volume V , the total pressure P , the temperature T , and the molal concentrations c_1, c_2, \dots, c_n , of each of the n constituents present. These variables are related by the equation defining concentration as

$$c_i = m_i/V,$$

where m_i is the number of moles of constituent i in the gas mixture, and the equation of state for a gas, which may be written

$$P = R \cdot T \sum c_i.$$

Which of these variables are to be regarded as independent depends upon the particular transformation under consideration. Other properties of the system such as its total mass M , its total energy E , its total entropy S , etc., will also be involved, but these are usually dependent variables. The total volume V , unquestionably should be an independent variable, since it is the only one which is always known without ambiguity. Next, in order of uncertainty, is the total pressure P , which, if we assume it to be hydrostatic pressure, can be measured with reasonable precision at any instant during the transformation in question. At this point an important

assumption must be introduced before further progress in the discussion is possible.

If definite meaning is to be attached to the temperature and concentrations, it is necessary to assume that the system is homogeneous, all components being in the gaseous phase and the properties either uniform or else varying continuously throughout the region. Therefore the system must either be in thermal and chemical equilibrium and the temperature and concentrations uniform throughout, or else it must be possible to assign to these variables average or effective values, with which are associated values for the total pressure, mass, energy, entropy, etc., which agree with the true values of these dependent variables within satisfactory limits. Such experimental investigations as those of Withrow, Lovell, and Boyd,²³ Spanogle and Buckley,²¹ Erichsen,³ and Rassweiler and Withrow¹⁶ indicate very definitely that the concentrations and temperature are not uniform throughout the gases in an engine cylinder, at least during combustion and the early portion of expansion. Whether or not it is permissible to use average or effective values for the concentrations and temperatures is a problem which will be reserved for later discussion.

Certainly the conclusion is unassailable that, if the application of rigorous thermodynamic analysis to the combustion process cannot be accomplished without detailed consideration of temperature and concentration variations, the problem becomes exceedingly difficult. It is true that such analyses as those of Nägel,¹⁵ Flamm and Mache,⁴ Midgley,¹⁴ and Rosecrans,¹⁸ which take into account the variation of temperature and composition in a gas mixture during combustion, are reasonably satisfactory when applied to combustion in closed spherical or cylindrical vessels. But the oversimplification of the combustion process, which these analyses entail, makes them inadequate when considering the more complicated process of combustion in the cylinder of an engine. For here the volume is very irregular in shape and changing with time, the gases are in turbulent motion, and heat loss to the walls is an important factor. The photographic investigations of Rassweiler and Withrow¹⁷ and of Rothrock²⁰ furnish convincing evidence of the complexity of the motion of the burned and unburned gas during combustion in an engine, and indicate that a rigorous analysis would probably involve hydrodynamics, with turbulent motion and heat conduction, as well as thermodynamics. Herzfeld¹¹ has analyzed the combustion and expansion processes in a very complete manner, including the effects of turbulence and heat transfer, but this analysis, even though extremely involved, still requires num-

erous questionable simplifying assumptions, for which it is difficult to find experimental verification.

An experimental investigation of gas temperature in the cylinder of an engine was undertaken at the University of Illinois in order to supply definite information with regard to such questions as those which have been mentioned above. The procedure has been to measure the gas temperatures at a series of points in the cycle during combustion and the first part of expansion, and to compare these observed values with values calculated by the method presented by Goodenough and Felbeck.⁶ Since the results of this investigation have been published previously,¹⁰ they will be very briefly reviewed in the present discussion, and attention will be given principally to their interpretation in the light of more recent investigations.

Measurement of Gas Temperatures in an Engine

The various methods of measuring gas temperature in an engine have been given detailed consideration in a previous paper.⁸ Therefore it is only necessary to state that, as a result of such consideration, the spectral-line-reversal method appears to be the only one which may be used satisfactorily to determine these temperatures. The chief advantages of this method, in addition to its simplicity, are the extremely small size and wide dispersion of the thermometric bodies, the radiating atoms, as well as the substantial amount of experimental information which is available regarding the precision and limitations of the method. Erichsen³ has recently used a spectroscopic method of temperature measurement, in connection with an investigation of combustion in a Diesel engine, for which he claims certain advantages over the line-reversal method. However, the method depends upon the emission of a continuous spectrum of pure temperature radiation which, as the investigations of Withrow and Rassweiler²⁴ have clearly demonstrated, is not the case in an engine operating on an Otto cycle.

The comparison of the maximum combustion temperature found from line-reversal measurements with those obtained by calculation for a wide range of air-fuel ratios shows rather unsatisfactory agreement.¹⁰ Throughout the normal operating range of air-fuel ratios of between 12 to 1 and 15 to 1 the calculated values are approximately 600°F. higher than the measured values, and with both richer and leaner mixtures the difference increases, reaching a maximum of 1000°F. at the lean combustion limit. In order to

determine, if possible, the cause of this disagreement, it is advisable to consider some of the different factors which may affect both measured and calculated temperature values.

The factors affecting the measured temperature may be divided into two groups as follows:

- (a) Experimental errors inherent in the method of temperature measurement: nonthermal excitation of radiation from the sodium atoms; absence of thermal equilibrium between the gases and the sodium atoms; cooling effect of the sodium solution entering with the fresh charge.
- (b) Experimental errors in the method as applied to engine temperature measurements: deposit or film on the cylinder windows; finite time of stroboscopic shutter opening.

The separate effects of the various sources of error listed above under (a) have been considered in previous publications^{10,8} and, on the basis of the results of numerous investigations of the temperature of stationary flames, the conclusion was reached that the combined effect of these errors could not result in such differences as those found between measured and calculated temperatures. A similar conclusion resulted for the sources of error listed under (b) above. Brevoort¹ has recently made a comprehensive study of the effect of fogging of the cylinder windows on line-reversal temperature measurements, and has found that the deposit which accumulates on the window in 200 min may raise the apparent temperature by more than 550°F. In the measurements discussed above, however, it was found that mounting the windows flush with the cylinder wall reduced fogging to such an extent that no appreciable error resulted if a lamp-temperature calibration was made immediately after each test.

Therefore it becomes necessary to examine critically the method of calculating the temperatures, for factors which might contribute to the difference between the measured and calculated values. Here again two distinct sources of error exist:

- (a) Inaccuracies in the method: incorrect thermal and chemical data for the gases under consideration; disregard of certain dissociation products.
- (b) Departure of operating conditions from assumed conditions for temperature calculations: absence of thermal and chemical equilibrium in the gases; departure from adiabatic, constant-volume combustion; temperature gradients in the gases.

The temperature calculations were originally carried out with the specific heat and equilibrium data of Goodenough and Felbeck,⁶ which were based on the results of calorimetric and chemical experiments. Much more accurate and reliable data, based on spectroscopic experiments, are now available.^{12,13} However, the recalculation of some of the temperatures, on the basis of these new thermal data, leaves them practically unchanged. This is due to some rather fortuitous compensating errors in the Goodenough and Felbeck data, which result in nearly the same energy at high temperatures for the two principal constituents, water vapor and carbon dioxide, with either set of specific heat data. Failure to consider the dissociation of H_2O into neutral OH, in the original calculations, was found to lead to temperatures which are about 150°F too high, but disregarding dissociation into monatomic gases and the formation of oxides of nitrogen had little effect.

The real crux of the matter would appear to be the absence of either thermal or chemical equilibrium. The only satisfactory evidence that the gases are in some kind of stable state is the fact that it is possible to produce a reversal of the spectral line. Whenever there is an insufficient amount of sodium being excited, the dark or reversed line cannot be made to appear. Such a condition exists when there is insufficient sodium present in the gases, or when, as during the early part of combustion, only a small amount of the sodium actually present is being excited. When either of these conditions obtains, accurate temperature measurements are impossible. This does not mean that the temperature is uniform throughout the region whenever reversal can be observed; but the reproducibility of the measurements is evidence of the establishment of a definite effective thermal stage in the gases, which exists, with only slight variations, at the same point in numerous successive cycles. von Elbe and Lewis²² have considered the problem of the thermal equilibrium following combustion in closed vessels, and have suggested that a delay in the distribution of energy over the molecular vibrational degrees of freedom would serve to explain some of the observed phenomena. However, if the sodium atoms are excited by collisions with the heated gas molecules, such an explanation would require that the measured temperatures be higher than the temperatures calculated, assuming complete equilibrium. Kühl¹² discusses briefly the effect of chemical reaction rate on the attainment of chemical equilibrium during combustion in an engine, but advances no experimental evidence, his conclusions being largely speculative.

There remains for consideration the influence

of heat loss and temperature gradient on the measured temperatures. In calculating the temperatures the effect of both of these factors was disregarded, but they must certainly influence the measured temperatures. From the temperature measurements of Rassweiler and Withrow¹⁶ it is possible to estimate the magnitude of the temperature gradients which may exist in the gases in an engine cylinder, while from the results of Griffiths and Awberry⁷ for reversal measurements with several flames at different temperatures, the effect of temperature gradient on these measurements may be estimated. On this basis it would seem reasonable to add a temperature gradient correction of from 150° to 200°F to the measured temperatures. Such a correction, together with the lowering of the calculated temperatures by a similar amount, owing to dissociation to form OH, would leave a difference of some 300°F between measured and calculated temperatures over the normal range of air-fuel ratios. From the results of calculations of heat loss, which were presented in an earlier publication,¹⁰ this would not appear to be an excessive temperature drop to be attributed to heat loss during combustion.

Summary

After considering the most likely factors which may influence the measurement and calculation of gas temperatures in an engine during combustion and expansion, there appears to be reasonable agreement between measured and calculated results if (1) temperatures are measured by means of the line-reversal method with suitable corrections for the effect of temperature gradients in the gases, and (2) temperatures are calculated on the basis of thermodynamic analysis, assuming thermal and chemical equilibrium, including the effects of variable specific heat of the gases and dissociation, based on the most recent thermal and chemical data, and correcting for heat loss during combustion.

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A MOLLIER DIAGRAM FOR THE INTERNAL-COMBUSTION ENGINE

H. C. HOTTEL AND J. E. EBERHARDT

Massachusetts Institute of Technology, Cambridge, Massachusetts

The limitations of thermodynamics as a tool for studying chemical reactions have been so adequately emphasized in college courses in physical chemistry as to have convinced many automotive engineers that thermodynamic study of the combustion process in an internal-combustion engine can yield no really useful results, that the only way to study knock or combustion mechanism, for example, is to focus attention on experimental studies of rate. The inherent complexity of the thermodynamics of a combustion process carried out at varying total pressure and volume and at such high temperatures as to cause ten different molecular species to be present in appreciable proportions has constituted a further brake on the development of this tool, and the misleading conclusions drawn from oversimplified attacks of the problem have not helped.

Although no claim is made that a thermodynamic study will by itself solve such a problem as engine knock, nevertheless the high temperature level of the combustion process as encountered in engines makes chemical equilibrium more than usually important in relation to rate—and mechanism—studies. Whether a certain combustion process is initiated in a far corner of the chamber ahead of the flame front will depend on the temperature and pressure existing there, which in turn are susceptible of prediction by a thermodynamic treatment of what has occurred in the rest of the chamber. It will be shown that the inherent complexity of a precise thermodynamic treatment of combustion may be reduced to a simple graphical procedure, which will be illustrated by the calculation of the performance of a conventionally "ideal" engine, and by the study of flame movement, temperature, and pressure in an unconventionally "ideal" engine in which combustion occurs during piston movement.

The steam engineer has long been familiar with the use of diagrams representing the thermodynamic properties of steam, and with the advantages of such diagrams for clarifying and simplifying the analysis of the operation of steam power-generating equipment. In the field of internal-combustion engine operation there is the same possibility of use of diagrams. If the quantity and atomic composition of a gaseous mixture are specified, the phase rule tells us that the specification of two properties is sufficient to fix completely all the other thermodynamic properties of the mixture. Consequently all the significant properties can be put on a single plot analogous to the Mollier diagram for steam; and

the tedious allowance for variation in specific heat with temperature and for shift in chemical equilibrium can be made *once and for all* during the construction of the chart. The solution of such problems as the determination of the maximum possible efficiency of a particular engine cycle is then as simple as the use of the Mollier diagram by the steam engineer. Important differences exist, however, between the plot for steam and for the working fluid of an internal-combustion engine. In the latter there must be a separate plot for each air-fuel mixture ratio of interest. Furthermore, the mixture prior to combustion is in physical but not chemical equilibrium, and separate charts are necessary for the unburned and the burned mixture. The combustion process itself involves a transfer from one chart to the other.

Diagrammatic Representation of the Working Fluid

A survey of the literature proved that the idea of representing equilibrium products of combustion on diagrams was not new. In 1932 Pflaum¹⁴ presented such diagrams plotted with enthalpy and entropy as coordinates; the omission of lines of constant internal energy introduced the necessity for trial and error in many calculations of interest. Pflaum also used thermal data which have since been improved enormously in accuracy, and made inadequate allowance for the complexity of the dissociation process. Subsequent to the completion of most of the present calculations Tanaka and Awano¹⁷ and Kühl¹⁰ have published additional diagrams. Tanaka and Awano followed Pflaum's example in the use of old thermal data, in allowance for dissociation, and in presentation of results on the enthalpy-entropy plane. Kühl, however, used modern fundamental data and made allowance for all important molecular species formed due to dissociation. Although diagrams of the types presented by these authors are of enormous assistance in the calculation of an engine cycle, all of them are characterized by the necessity for a considerable amount of algebraic calculation and of trial-and-error methods of solution.

The thermodynamic properties of interest are temperature T , entropy S , enthalpy H , internal energy E , pressure P , and volume V . Since $H = E + PV$ one of these latter four could in theory be omitted, but experience in the solution of various combustion problems indicates that freedom from trial and error necessitates includ-

ing them all. The calculation of the relations among these six properties requires certain basic thermodynamic data: namely, certain equilibrium constants as functions of the temperature, certain heats of reaction, and the specific heats of the various molecular species as functions of the temperature. The data need not be directly available in just these forms; it is sufficient if these data or certain other data (for example, entropies), related to them by any of a number of thermodynamic expressions, are obtainable.

In recent years the technique of calculating the specific heats of gases over a temperature range extending down to absolute zero has been perfected; the calculations have been carried out for a number of gases, and the results have been published in a series of papers by Johnston and his coworkers,^{1,4-8} and in papers by Kassel⁹ and Gordon,² all of which appeared in the years 1933, 1934, and 1935. Knowledge of the specific heats permits the calculation of entropies; the results of these calculations are given in the papers mentioned. The high precision of the fundamental spectroscopic data used in these calculations and the excellent agreement between these new specific heats and those obtained from recent and refined experimental determinations substantiate the belief that no significant revisions of these values need be expected in the future.

The sources of the internal energy and entropy values for the various molecular species involved in the present work, and the methods used in evaluating changes in internal energy and entropy for the various chemical reactions involved,

are summarized in Tables 1A and 2A of a previous paper by Hershey and the present authors.³ The equilibrium constants used are those summarized by Lewis and von Elbe.¹²

The fuel chosen as adequately representative of gasoline is octane, C_8H_{18} ; [it is recognized that the trend in motor fuel quality is towards lower proportions of paraffinic stock; the difference between $(CH_{2.25})_x$ and $(CH_2)_x$ is unknown, but for most thermodynamic calculations it is believed unimportant] its hydrogen-carbon ratio, rather than its molecular weight, is its significant characteristic for the present purpose. The air-fuel ratios chosen for study were three, corresponding to a rich mixture (85 per cent of the theoretical air or 117.6 per cent of the theoretical fuel), a mixture in proportion for perfect combustion, and a lean mixture (110 per cent of theoretical air, or 90.9 per cent of theoretical fuel).

The first problem in the construction of a chart of the burned gases is the determination of the composition of a mixture containing carbon, hydrogen, oxygen, and nitrogen, which is in chemical equilibrium at the conditions specified. Because of the high temperature attained in internal-combustion engines, the number of different kinds of molecules existing in important proportions in the products is much larger than in free-burning flames in furnaces. Preliminary calculations indicated that the products would contain carbon dioxide, water vapor, nitrogen, oxygen, carbon monoxide, hydrogen, OH, H, O, and nitric oxide, the relative importance of the

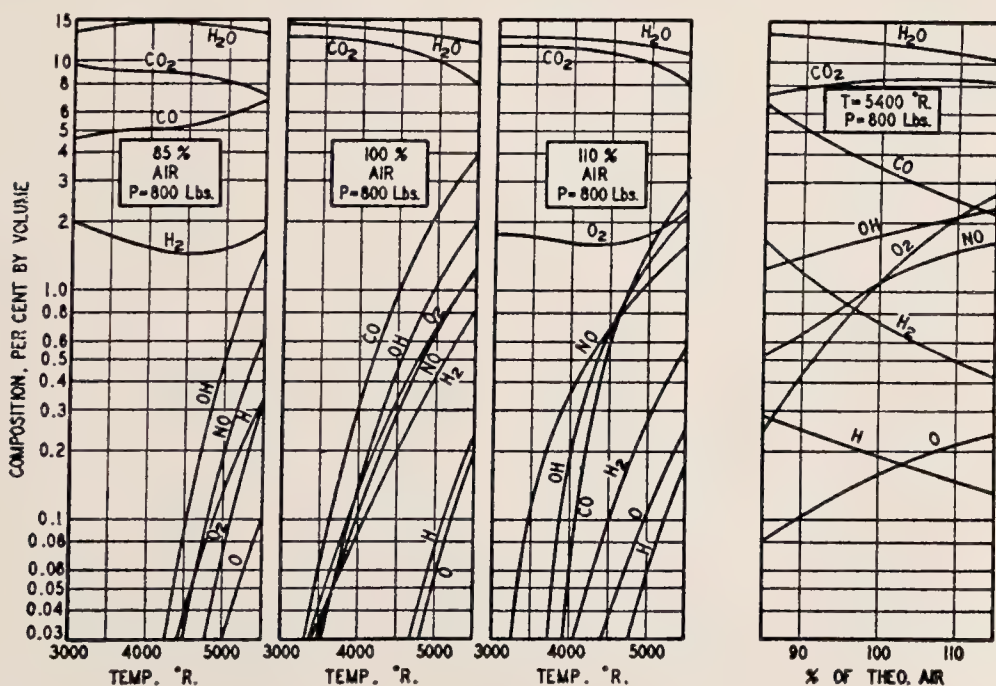


FIG. 1. Effect of air-fuel ratio and temperature on composition of combustion products.



SCALE FOR HORIZONTAL INTERPOLATION BETWEEN PRESSURE OR VOLUME LINES

- E = Total internal energy, Btu
 E_s = Internal energy, exclusive of internal energy of combustion
 H = Total enthalpy, $E + PV$ (144/778), Btu
 $H_s = E_s + PV$ (144/778), Btu
 P = Pressure, psi (dashed lines)
 V = Volume, cu ft (solid lines)
 S = Total entropy, Btu/°R
 T = Temperature, °R (°F + 460)
 Base = 60°F, complete combustion (see text)
 Fuel = $(CH_{2.25})_x$

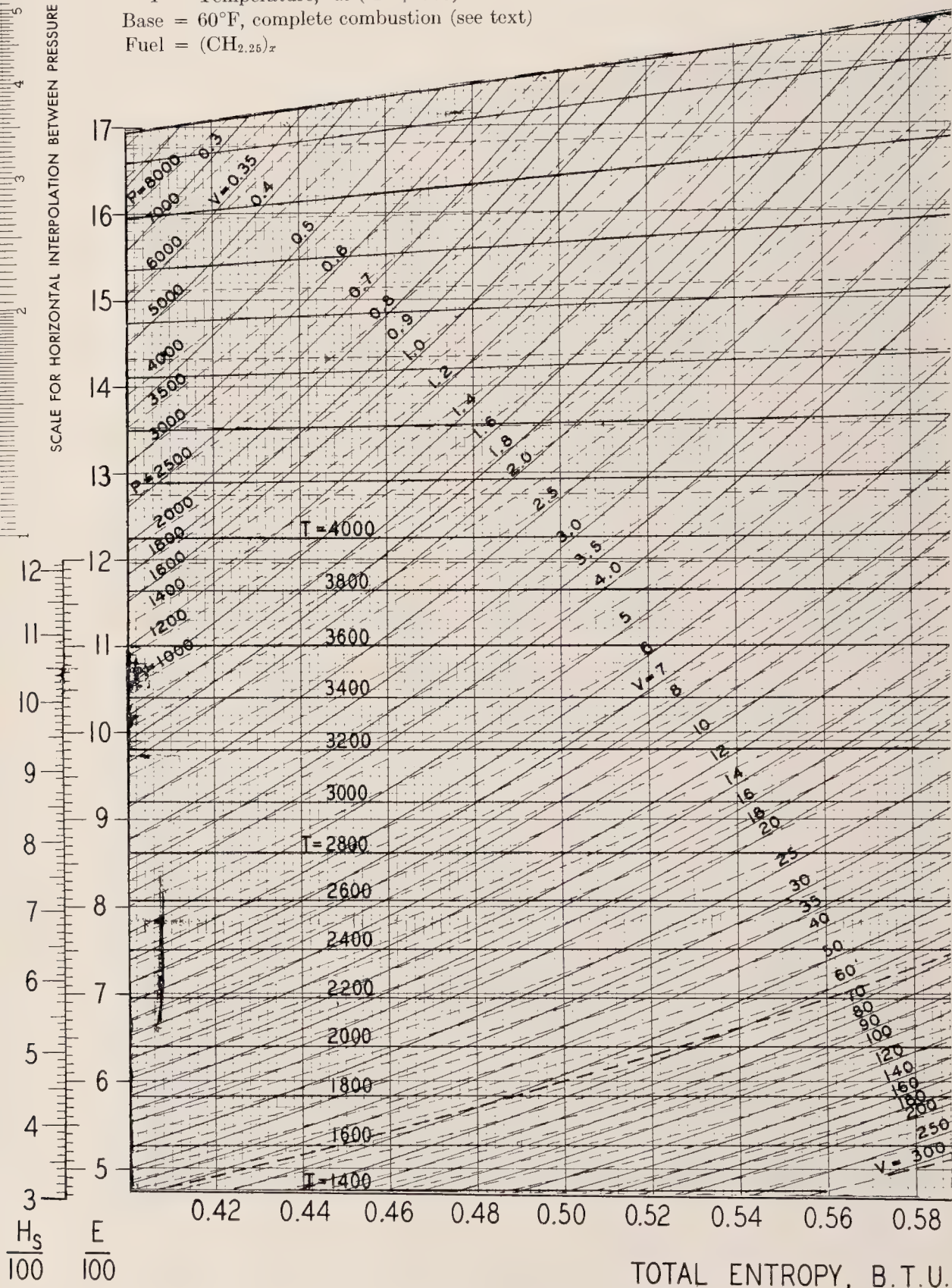


FIG. 2. Thermodynamic properties of the products of combustion of

various species depending on the temperature, pressure, and mixture ratio. The method of using data on equilibrium constants to calculate the composition of the products is presented in the reference previously cited.³

Typical results of such calculations for a total pressure of 800 psi on the system are presented in Fig. 1, showing the effect of temperature on gas composition for each of three mixture ratios (three plots on left). The importance of NO and neutral OH, frequently omitted from consideration in flame-temperature calculations, and even of atomic oxygen and hydrogen at the highest temperatures, is apparent from a study of the figure. The right-hand plot of Fig. 1 shows how a variation in air-fuel ratio affects the composition of the equilibrium mixtures, when the temperature and pressure are fixed at 5400° Rankine (°F + 460°) and 800 psi.

With compositions determined for various temperatures and pressures, the next step is the calculation of the various thermodynamic properties fixed by the state of the system, and the presentation of the results on diagrams, one for each mixture ratio under consideration. One such diagram is presented in Fig. 2, for a rich mixture containing 85 per cent of the required air for complete combustion (not far from the maximum-power mixture ratio). The material basis for the diagram is the quantity of material (C; H, O, N, in the ten molecular arrangements already mentioned) which contains nitrogen and oxygen equivalent to 1 lb of air. For Fig. 2 the weight of carbon plus hydrogen associated with the 1 lb of oxygen plus nitrogen is 0.0782 lb. Other similar diagrams have been constructed for the lean and the "theoretical" mixture.³

The thermodynamic properties represented on the diagrams, their symbols, units of measurement, and bases, follow:

(1) Temperature T , in degrees Rankine, or degrees Fahrenheit + 460°; almost horizontal solid lines at 200-degree intervals.

(2) Volume V , in cubic feet; diagonal solid lines.

(3) Pressure P , in psi; diagonal dashed lines of gentler slope than the volume lines.

(4) Internal energy E , in Btu, the vertical scale of the diagram. This property is the heat effect attending the conversion, at constant volume and consequently without work, of a mixture from its given condition of composition and temperature to carbon dioxide, water vapor, oxygen, and nitrogen at the base temperature of 60°F (520° Rankine). Although any path may be chosen in the calculations underlying the construction of the chart, that one simplest to visualize involves cooling the mixture at constant

volume to the base temperature, thereby evolving what may be called the sensible internal energy content E_s , of the mixture, then allowing the mixture to react at constant temperature and volume to produce only carbon dioxide, water (vapor), nitrogen, and oxygen. The heat evolved along this second leg of the path, the internal energy of combustion at the base temperature, is added to the first quantity to give E .

(5) Enthalpy or total heat H in Btu; almost horizontal dashed lines found only in the upper portion of the diagram. By definition, $H = E + PV$ (144/778).

(6) Entropy S in Btu/°R, the horizontal scale of the diagram. Calculated by assigning zero entropy to carbon dioxide, water vapor, oxygen, and nitrogen at 14.7 psi each and 60°F (520°R). The entropy of any other gas at the base temperature is then equal to its entropy of formation from the preceding constituents of zero entropy. For further quantitative consideration of the entropy concept, essential to an understanding of the technique of calculating the diagrams but not to their intelligent use, the reader is referred to any standard textbook on thermodynamics.

(7) Sensible internal energy E_s in Btu. This property already has been defined in the discussion of E . In the lower temperature range of Fig. 2, where the chemical composition of the mixture is fixed by temperature alone [because the only chemical reaction possible is the water-gas reaction, $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$, which is unaffected by pressure], the value of E_s is determined completely by E . Consequently the sensible internal energy is given by the vertical scale on the lower right margin of the diagram, relating E_s and E . The difference between E and E_s is the internal energy of combustion of the carbon monoxide and hydrogen present by virtue of the insufficiency of air.

(8) Sensible enthalpy or sensible heat H_s in Btu. By analogy with H , $H_s = E_s + PV$ (144/778). Like E_s , H_s is a unique function of E at low temperatures and consequently representable by a scale which appears in the lower left margin of the diagram. [It is to be noted that $(H - H_s)$ is equal to $(E - E_s)$ and, consequently, to the E of combustion at the base temperature, not to the H of combustion. This is a consequence of the choice of basis of the plots, which makes E_s , not H_s , zero at the base temperature.]

The illustration of the uses of Fig. 2 in the solution of various problems of combustion in engines must await a discussion of the corresponding diagram representative of the unburned mixture. The mixture prior to combustion consists in part of products of combustion of the

preceding cycle, and in part of a mixture of fresh fuel vapor and air. The two parts are, of course, identical in weight percentage of C, H, O, and N. In order that the diagram presenting the properties of the unfired gas shall be on the same material basis as that previously discussed, the basis will again be 1 lb of oxygen plus nitrogen, and 0.0782 lb of carbon plus hydrogen. Simple stoichiometric calculations show that this would form 0.0392 lb.-mole if present as combustion products (nitrogen, carbon dioxide, water vapor, carbon monoxide, hydrogen) or 0.0354 lb.-mole if present as air and octane vapor. Let the weight fraction of the mixture existing as unpurged combustion products of the previous combustion cycle be represented by f , the weight fraction brought in as fresh air and octane vapor by $(1 - f)$. Then the diagram to be constructed representative of the unfired gas must correspond to a number of moles given by $0.0392f + 0.0354(1 - f)$, or $0.0354 + 0.004f$. The base temperature is 60°F, as before, and the desired thermodynamic quantities, in general, are the same. However, since the diagram is to be used to calculate adiabatic changes that are physically but not chemically reversible, the entropy basis must be defined to omit chemical contributions to entropy; zero entropy is therefore assigned to each constituent at 60°F (520°R) and 14.7 psi. The total internal energy E is, as before, the sum of two quantities, the sensible internal energy E_s and the internal energy of combustion E_C at the base temperature (fuel and products both

as vapor). The former is the heat effect attending the constant-volume cooling to the base temperature without chemical reaction. Since both the number of moles and the specific heat are very insensitive to variations in f , E_s may be evaluated for some mean value of f and used with negligible error even though f varies considerably from the value used.

The internal energy of combustion E_C , on the other hand, changes greatly with f . For the rich mixture under discussion E_C will be $(1 - f)$ times the internal energy of combustion of 0.0782 lb of octane, plus f times the internal energy of combustion of any hydrogen and carbon monoxide in the products of combustion. Taking the lower heat of combustion of octane at constant volume at 60°F as 19,270 Btu per pound and of the carbon monoxide and hydrogen associated with the products of combustion of 1 lb. of air as 300 Btu ($E - E_s$ as read from Fig. 2), the quantity E_C equals $300f + (1 - f) 19,270 \times 0.0782$. Since E_s , but not E , is substantially independent of the fraction f of unpurged combustion products in the system, the diagram representative of the unfired mixture, Fig. 3, is made with vertical scales of sensible internal energy E_s . The total value E is obtained by adding to E_s the internal energy of combustion, readily calculated when f is known.

Since in the unfired mixture no chemical changes are occurring, the internal energy E_s is a unique function of T . Accordingly a scale on the right of the diagram relates these quantities.

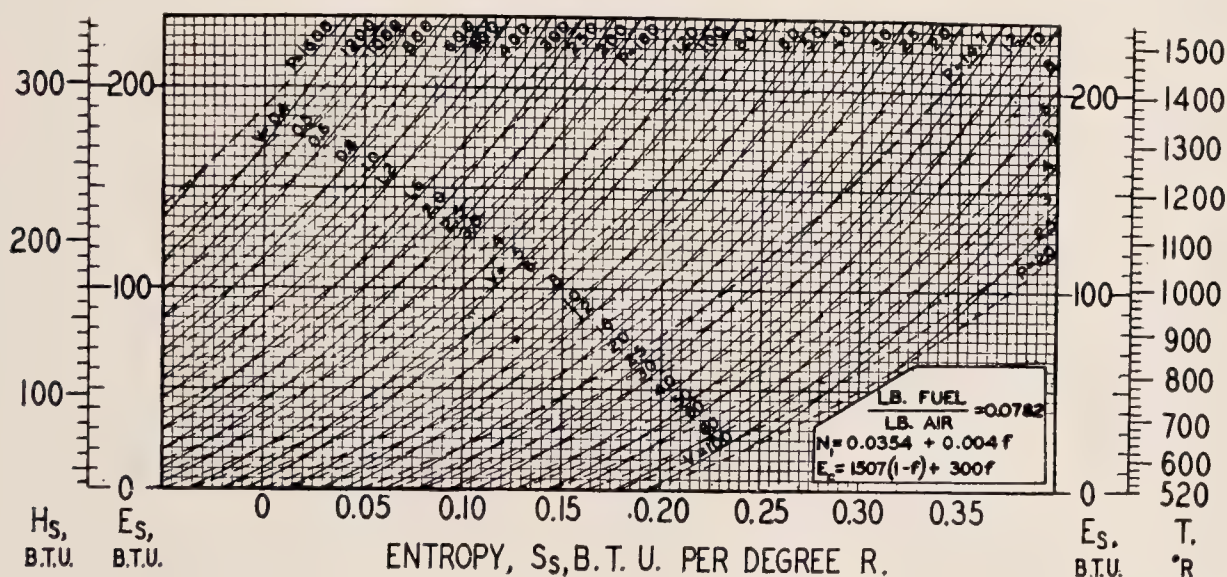


FIG. 3. Thermodynamic properties of a rich mixture of air and octane vapor, plus unpurged combustion products, before firing. E_s = internal energy exclusive of internal energy of combustion, in Btu; $H_s = E_s + PV$ (144/778) in Btu; S_s = entropy exclusive of entropy of combustion; P = pressure in psi (dashed lines); V = volume in cubic feet (solid lines); T = temperature in degrees Rankine ($= ^\circ\text{F} + 460$); base = 60°F (see text); fuel = octane, C_8H_{18} ; f = weight fraction of charge left in clearance volume (see text).

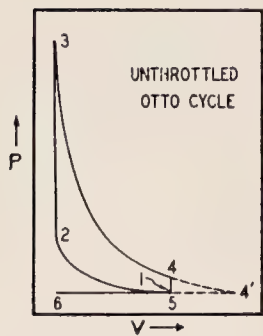


FIG. 4. Ideal indicator diagram for unthrottled Otto cycle

Similarly a scale on the left relates

$H_s [= E_s + PV(144/778)] \text{ and } E_s.$

The method of using Fig. 3 representing the unfired gas, referred to hereafter as the “unburned” chart, and Fig. 2, referred to as the “burned” chart, will now be illustrated by examples.

Efficiency and Mean Effective Pressure of Ideal Otto Cycles

Let it be desired to study the thermodynamic limitations on power output and mean effective pressure when an Otto cycle engine is operated using octane with 85 per cent of theoretical air, with a compression ratio of 6, the intake and exhaust manifold pressures atmospheric, and the fuel-air mixture leaving the carburetor completely vaporized and at 90°F. Figure 4 represents an indicator diagram for the ideal cycle. Reference to the successive states of the system will be made by appending subscripts corresponding to the numbered points on the diagram. Because of the relation of a cycle to that preceding it, it will be necessary temporarily to assume knowledge of two quantities, and these are most conveniently T_1 , the temperature of the mixture of fresh and unpurged gas prior to compression, and f , the fraction of the gas from the preceding cycle left in the cylinder prior to the intake stroke. These will be assumed to be 650°R (190°F) and 0.05, respectively; they may be checked readily later.

Step 1-2, compression of the charge. On Fig. 3, the right-hand scale indicates that when $T_1 = 650^\circ\text{R}$, E_{S1} equals 26 Btu. On the diagram locate the condition 1, corresponding to $E_{S1} = 26$ and $P_1 = 14.7$ psi (heavy dashed line). From the diagram read $V_1 = 16.8$ cu ft. Since Step 1-2 is an adiabatic reversible compression and consequently isentropic, move vertically on the diagram from V_1 to $V_2 (= 16.8/6 = 2.8$ cu ft). From the diagram, read $E_{S2} = 138$ Btu.

Step 2-3, adiabatic combustion at constant volume, $V_3 = V_2 = 2.8$. At point 2 the total internal energy E_2 equals the sum of the sensible value E_{S2} and the chemical value of E_{C2} , which latter value is $1507(1 - f) + 300f = 1507 \times 0.95 + 300 \times 0.05 = 1447$. Then the total $E_2 = 138 + 1447 = 1585$ Btu. Since combustion occurs at constant volume and is adiabatic, there is no change in internal energy. Therefore, $E_3 = 1585$ and $V_3 = 2.8$, permitting the location of a point on the diagram representing the combustion products in chemical equilibrium, Fig. 2. For convenience in subsequent use of Fig. 2, the entropy S_3 will be recorded; it is 0.576.

Step 3-4, adiabatic reversible expansion, therefore isentropic, to $V_4 = V_1 = 16.8$. Move vertically downward along the entropy line $S = 0.576$ of Fig. 2 from $V_3 = 2.8$ to $V_4 = 16.8$, and read $E_4 = 1010$.

Step 4-5, opening of exhaust valve and release of pressure to atmospheric. Although this step is irreversible, if all pressure drop is assumed localized at the exhaust port, then that portion of the charge remaining in the cylinder may be considered to have undergone an adiabatic reversible expansion, doing work on the gas flowing through the port. The condition of the mixture at point 5 then corresponds to point 4' on the dotted portion of the diagram, Fig. 4. Move down vertically on $S = 0.576$ of Fig. 2 to $P_{4'} = 14.7$ psi, the heavy dashed line, and read $E_{4'} = 723$ and $V_{4'} = 66$, and from the scale on the left, $H_{S4'} = 610$. These quantities correspond to an amount of material equal to the whole charge, whereas only the fraction $V_5/V_{4'} = 16.8/66$ or 0.255 of it is left in the chamber.

Step 5-6, expulsion of all but the fraction V_6/V_5 of the remaining gas at constant pressure. This step leaves $V_6/V_{4'}$ or $2.8/66$ or 0.0424 of the original charge in the cylinder. This is the fraction f , assumed to be 0.05 at the beginning of the calculation.

Step 6-1, mixing of the unpurged gas f with $(1 - f)$ of fresh fuel-air mixture as the piston moves to bottom dead center. Since this step occurs at constant pressure the total H is constant, and since no chemical reaction is occurring, H_s is constant. Therefore, the sensible heat of the unpurged residue (which still corresponds in condition to that at point 4' where H_s equalled 610) plus that of the entering fresh charge must equal that of the mixture at point 1. From Fig. 3, a fresh charge at 90°F (550°R) has an E_s of 6 (right-hand marginal scale) and an H_s of 43 (left-hand marginal scale).

Then

$H_{S1} = 0.0424 \times 610 + 0.9576 \times 43 = 68 \text{ Btu.}$

From Fig. 3, when $H_s = 68$, $E_s = 23$, and $T = 640^\circ\text{R}$.

This constitutes a check on the value originally assumed for T_1 , namely, 650°R . Although this whole calculation could now be repeated with the better values for T_1 and f , the changes resulting therefrom would be found small; they will be ignored in the present example. The next step is the calculation of thermal efficiency. The work of the cycle is $(E_3 - E_4) - (E_2 - E_1)$ and, since no chemical change occurred between 1 and 2, $E_2 - E_1 = E_{s2} - E_{s1}$. The work is, therefore, $(1585 - 1010) - (138 - 26) = 463$ Btu. This work is accomplished by the introduction of $(1 - 0.0424)$ lb of fresh air and $(1 - 0.0424) 0.0782$ or 0.0749 lb of fresh fuel. Adopting the conventional H of combustion of fuel as the denominator in the expression giving efficiency and using the value 19,240 as the net heat of combustion of octane vapor at constant pressure, one obtains for thermal efficiency,

$$\frac{463}{0.0749 \times 19,240} \times 100 = 32.1 \text{ per cent.}$$

The mean effective pressure in lb/ft² is equal to the net work of the cycle in foot-pounds, divided by the displacement volume in cubic feet

$$\text{m.e.p., in psi} = \frac{463 \times 778}{(16.8 - 2.8) \times 144} = 178.$$

For more precise calculation of mean effective pressure or volumetric efficiency it is recommended that V_1 be determined by use of the perfect gas law from the known values of T_1 , P_1 , and N_1 (the number of moles of charge for compression, obtained from f):

$$V_1 = 0.729 N_1 T_1 (14.7/P_1). \quad (\text{A})$$

The temperature and pressure at various points in the cycle may, of course, be determined from the charts during the calculation of the efficiency.

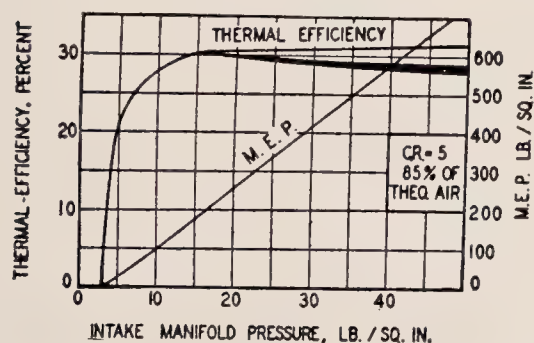


FIG. 5. Effect of intake manifold pressure on the efficiency and mean effective pressure of an Otto-cycle engine

The application of thermodynamic-property charts such as Figs. 2 and 3 has been illustrated elsewhere³ with numerical examples of the calculation of the performance of various other ideal engine cycles, including throttled, supercharged, variable-cutoff, compression-ignition, and gas turbines. Figure 5, summarizing some of that work, shows the calculated effect of intake manifold pressure, varied by throttling or supercharging, on the thermal efficiency. The efficiency increases rapidly from zero at 3 psi where the pumping loop and work-output loop exactly counterbalance. Above atmospheric intake pressure, the efficiency increases slightly with increased supercharging if the cycle is not charged with the work of supercharging. If the latter work is included, the efficiency drops off slightly at high supercharge pressures, the magnitude of the effect depending on the characteristics of the supercharger. (Isothermal and adiabatic supercharger operation, representing the limiting values, are indicated by two lines connected by a shaded area.) The mean effective pressure, on the same basis as the top curve of thermal efficiency, is shown in the same figure. The mean effective pressure is seen to increase substantially linearly with intake manifold pressure.

Effect of Flame Travel Across the Combustion Chamber

The problem previously considered was simplified to the extent of assuming that combustion took place instantaneously, yielding homogeneous combustion products. Use of the charts will now be made to illustrate the effect, on the pressure-temperature-space-time relations, of the travel of the flame across the combustion chamber. The first example to be considered will be that of combustion occurring at constant total volume (e.g., in a bomb or at top dead center in an engine). Later examples will illustrate the effect of the motion of the piston.

As a flame passes through a confined mass of gas-air mixture the pressure rises continually, the burning of an infinitesimal amount being accompanied by an infinitesimal rise in pressure. Any given element of the gas-air mixture, then, burns at constant pressure or constant enthalpy. As the combustion progresses, both the burned gas behind the flame front and the unburned gas ahead of it are compressed isentropically if no heat is lost. Since flame velocities are low compared to the velocity of sound, the pressure may be assumed uniform throughout the mass. Flame velocities are high, however, relative to the velocities of any eddy currents set up by the passage of the flame, so that mixing should be

relatively slight. Furthermore, heat transfer by conduction alone is negligible in the time of passage of flame through a charge. In the limit, then, each element of gas may be assumed to undergo an isentropic compression from its original state as the flame moves towards it, a combustion at constant pressure when the flame reaches it, and a further isentropic compression as the flame moves on into the unburned part of the charge.

A statement of the problem and of the basic assumptions follows: A confined gas-air mixture is ignited and, as the flame is propagated, the total volume is held at a constant value and there is no external heat loss, no mixing, and no heat flow between adjacent elements of gas. Pressure gradients throughout the mass are negligible. The relations to be found are: (a) the relation between the mass-fraction burned and the pressure, and (b) the temperature distribution through the mass at any time.

Nomenclature

The numerical values of all extensive properties are to be those corresponding to the basis of the property charts.

E_{p_0} , in Btu = initial internal energy of unburned gas-air mixture at the original pressure p_0 .

c = mass fraction of the charge burned when the pressure has reached the value p_c .

E_{p_c} , in Btu = internal energy of the unburned gas-air mixture after isentropic compression from the initial pressure p_0 to the pressure p_c .

x = mass-fraction position of the element which burned when the pressure was p_x .

$E_{p_x p_c}$, in Btu = internal energy of that element of the burned gas at the pressure p_c which has a mass-fraction position x , or which has reached pressure p_c along the path: isentropic compression of the unburned gas-air mixture from the initial p_0 to p_x , combustion at the constant pressure p_x , isentropic compression of the burned gas from p_x to p_c . [Note that the single pressure subscript on E denotes unburned gas and the double pressure subscript denotes burned gas.]

The initial internal energy of the system is E_{p_0} and, since the combustion is to take place at constant total volume, the internal energy of the entire system must remain constant at this value, although it will be composed of elements having different energies. When the fraction c of the charge has burned the pressure has risen to the

value p_c , and the internal energy of that portion of the charge as yet unburned will be

$$E_{p_c}(1 - c). \quad (1)$$

The energy of the burned portion of the charge is more difficult to evaluate, since there is a continuous variation in energy throughout it. By the definition of $E_{p_x p_c}$ the energy of the burned portion is:

$$\int_0^c E_{p_x p_c} dx \quad (2)$$

The sum of this integral giving the energy of the burned portion and the energy of the unburned portion must equal the constant energy of the system, or

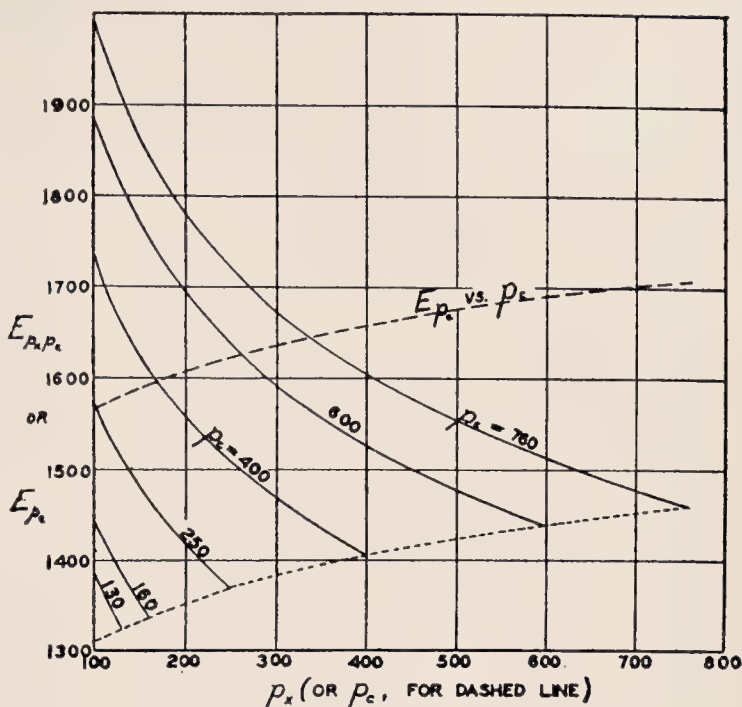
$$E_{p_c}(1 - c) + \int_0^c E_{p_x p_c} dx = E_{p_0} \quad (3)$$

The solution of Eq. (3) would be extremely difficult without the thermodynamic property charts except by the use of unwarranted simplifying assumptions. Even with the charts its use is difficult without certain working plots which will now be described.

Figure 6 presents (single dashed line) the relation between E_{p_c} and p_c . The construction of this curve follows simply from the "unburned" chart (Fig. 3). Since, by definition, E_{p_c} is the internal energy of the unburned mixture after isentropic compression from its initial state, the intersections of the pressure and energy lines at the entropy of the initial gas-air mixture determine the curve of E_{p_c} versus p_c . The "sensible" energy will be read from the chart, and E_{p_c} is the sum of this value and the energy of combustion.

The family of curves in Fig. 6 represents $E_{p_x p_c}$ versus p_x for various constant values of p_c . These curves must be obtained from the "burned" chart, Fig. 2. The evaluation of any point on these curves must be carried out as described in the definition of $E_{p_x p_c}$. At a given pressure p_x , the properties of the unburned gas are read from the "unburned" chart, Fig. 3, at the initial entropy. In this case H_S is the only property of interest. The energy of combustion is to be added to the value of H_S as read from the chart, giving H . Since by definition of $E_{p_x p_c}$ the gas must be burned at the constant pressure p_x , or the constant value of H just found, a point may be located on the "burned" chart, Fig. 2, at these values of p and H and the corresponding value of internal energy read. This value is $E_{p_x p_c}$ for $p_x = p_c$. Values of $E_{p_x p_c}$ for the same value of p_x and for other values of p_c may be located by moving along a line of constant entropy from the value just found.

FIG. 6. Relation between E_{pc} and p_c (single dashed line) and between E_{pxpc} and p_x for different constant values of p_c (solid lines). (See table of nomenclature.)



The technique of using Eq. (3) involves a stepwise calculation with the pressure p_c chosen as the independent variable. For the first step, if the value of p_c is chosen not greatly different from the initial pressure p_0 , the value of c to be found will be small and will be denoted by $\Delta'c$. Equation (3) may then be written:

$$E_{pc}(1 - \Delta'c) + (E_{pxpc})'_{Av} \Delta'c = E_{p_0} \quad (4)$$

in which $(E_{pxpc})'_{Av}$ indicates the average energy of burned gas at the pressure p_c which burned at pressures varying from p_0 to p_c . If the step is small and/or if the relation connecting c and p_c is substantially linear, $(E_{pxpc})'_{Av}$ is the average value of E_{pxpc} as obtained from Fig. 6 between $p_x = p_0$ and $p_x = p_c$ along the curve for the value of p_c chosen.

For illustration by means of a particular example, consider an engine with a compression ratio of 6.0 operating with a mixture ratio corresponding to 85 per cent of theoretical air and with $f = 0.042$, $p_1 = 14.7$, and $T_1 = 643^\circ$ (from which $V_1 = 16.5$) at the end of the compression stroke ($V_2 = 2.75$); one finds from Fig. 3 that $E_{S2} = 138$, $T_2 = 1155$, $p_2 = 160$, $H_{S2} = 220$, $E_2 = 138 + 1507(1 - 0.042) + 300(0.042) = 1594$, and similarly $H_2 = 1676$. Now let the charge be ignited at the conditions just specified, with the piston held at top dead center (volume constant at 2.75) while the flame sweeps through the combustion chamber. The relation between the mass-fraction burned and the pressure, and the temperature distribution through the mass are now to be calculated.

As outlined above, the first step involves the

choice of p_c which, for the present example, will be chosen as 250. From the dashed curve of Fig. 6, E_{pc} (for $p_c = 250$) = 1624. The average value of E_{pxpc} between $p_x = 160$ and $p_x = 250$ along the curve labeled $p_c = 250$ is 1414, which equals $(E_{pxpc})'_{Av} \cdot E_{p_0} = 1594$. Substitution of these values into Eq. (4) yields $\Delta'c = 0.143$, i.e., by the time the pressure has risen from 160 to 250, 14.3 per cent of the charge has been swept by flame.

For the second step Eq. (4) must be modified to:

$$E_{pc}(1 - \Delta'c - \Delta''c) + (E_{pxpc})'_{Av} \Delta'c + (E_{pxpc})''_{Av} \Delta''c = E_{p_0} \quad (5)$$

in which $(E_{pxpc})'_{Av}$ is now to be evaluated between the same values of p_x but along the curve for the second chosen value of p_c . $(E_{pxpc})''_{Av}$ is then the average E_{pxpc} between $p_x =$ the first chosen value of p_c and $p_x =$ the second chosen value of p_c , along the curve for the second chosen value of p_c . Since $\Delta''c$ is now the only unknown in Eq. (5), its value can be determined and added to $\Delta'c$ to give the total c up to this point.

For each successive step, corresponding new terms in Δc and $(E_{pxpc})_{Av} \Delta c$ must be added. It will be noted that each of the terms $(E_{pxpc})_{Av}$ will be obtainable from Fig. 6 by averaging along the p_c -curve over the pressure interval within which the corresponding increment burned.

The final results of this stepwise calculation are presented in Fig. 7 (solid line labelled "combustion without piston movement") as p_c versus c . It will be noted that the relation is found to

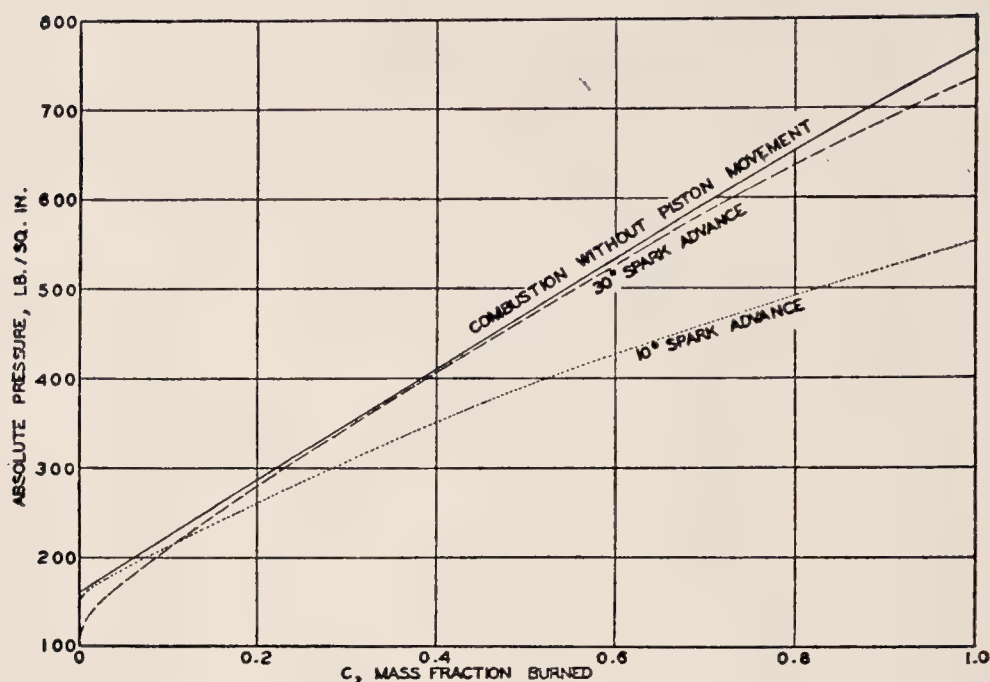


FIG. 7. Change of pressure with progress of combustion for three conditions of firing.

be substantially linear throughout, so that somewhat larger steps could have been taken without appreciable loss in precision. (The literature contains examples of studies of flame propagation based on this simplifying assumption of linearity between p_c and c .)

The final pressure is 765 psi, a value to be compared with the pressure 775 reached at point 3 in the previously discussed unthrottled Otto cycle where perfect mixing was assumed at all points. Obviously, if the products of combustion in the present example were thoroughly mixed, at constant volume, conditions would be identical with those at point 3 in the unthrottled Otto cycle example. This mixing would be accompanied by a slight rise in pressure because of the higher specific heat (including dissociation) at the higher temperatures. The phenomenon has been investigated by Mache¹³ and by Lewis and von Elbe,¹¹ the latter reporting changes in pressure up to 0.8 per cent for hydrogen-oxygen explosions. The small difference in the pressures indicates that calculations of the type just discussed should be predicated on interest in the temperature distribution through the mass rather than interest in the pressure after combustion. The calculation of the temperature distribution will now be discussed.

The temperature distribution for the present example is presented in the left half of Fig. 9 as temperature versus mass fraction measured from ignition point. The lowermost curve presents the temperature of the unburned gas ahead of the flame front. The points for this curve were obtained from the "unburned" chart, Fig. 3, by

reading the temperature along the isentropic path as a function of the pressure and obtaining the corresponding mass fraction from the p_c versus c plot just discussed. The middle solid curve represents the temperature attained at the instant of combustion of any given layer. Combustion at constant pressure or constant H provides a means of calculating these points from the corresponding points on the lower curve. The upper curve presents the temperature distribution at the end of combustion. Points for this curve are calculated from the corresponding points on the middle curve by isentropic compression to the final pressure, using Fig. 2. These curves will be discussed later in comparison with other results. The temperature distributions throughout the charge at various times during the combustion are shown by the dotted lines, the vertical portions showing the position of the flame front. (These results on flame propagation replace those given in Fig. 7 of Reference 3, which were obtained by a method there labeled an approximation.)

Part of the technique of making the calculations with allowance for piston movement is the same as that outlined above. Equation (3) [or (4) or (5)] is modified only to the extent of correcting the right-hand side for the change in the total energy of the system caused by the work done by the piston. This is simply the average pressure during one of the small steps, multiplied by the change in volume (with the proper sign). Care must be exercised if the piston goes through top dead center in one of the steps. However, Eq. (4) or Eq. (5), with the work cor-

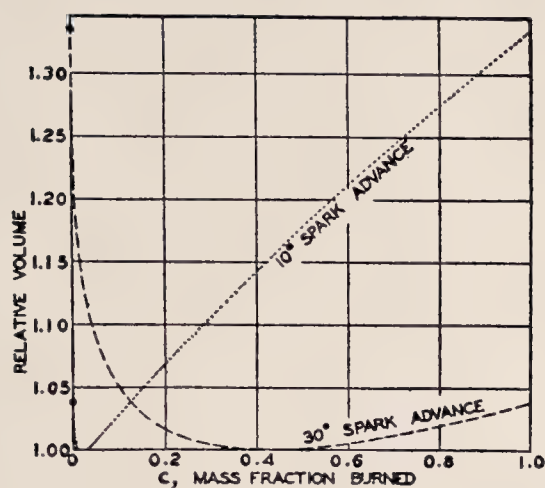


FIG. 8. Progress of flame in relation to piston movement

rection, is not sufficient in this case because the pressure-volume relation is not known in advance, and hence the work term is not fixed by the techniques of choosing p_c . Additional information related to flame speed—information which no purely thermodynamic analysis can hope to yield—is necessary. The most convenient form that this information can take is relation between c , the mass fraction burned, and crank

angle, readily converted to the relation between c and chamber volume, V . With this latter relation given, the calculation for a single step of the combustion process involves trial and error in finding those values of Δc and ΔV which will satisfy both Eq. (4) [or (5)], with the work term included, and the c - V relation.

For illustrative purposes two examples have been calculated, with ignition 30° and 10° , respectively, before top dead center. In both cases combustion was assumed to have been completed in 40° of crank revolution. As a fair approximation the fraction burned was assumed proportional to the cube of the time after ignition, or to the cube of the crank travel after ignition. This approximation was combined with the known relation of volume to crank angle to produce the curves of Fig. 8, giving the c - V relation for the two cases in question. Admittedly the relations presented in Fig. 8 represent an assumption, although data presented by Rassweiler and Withrow¹⁵ indicate that pressure is nearly cubic in time. The assumptions do not detract from the value of the examples as illustrations of a method.

The stepwise-calculated relations of pressure to fraction burned are presented in Fig. 7 as the dashed and dotted lines. Since ignition occurs before top dead center has been reached, com-

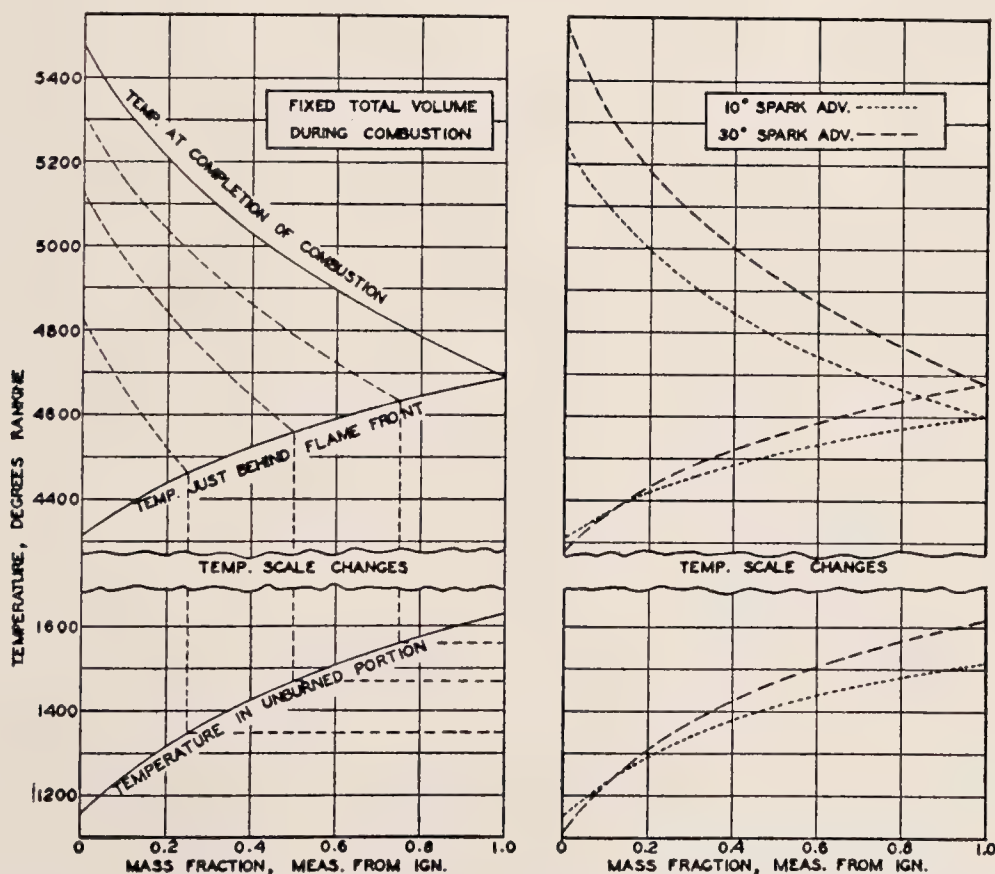


FIG. 9. Effect of flame travel on temperature in a combustion chamber. Left—chamber of fixed volume; right— 30° and 10° spark advance, with flame travel occupying 40° of crank revolution.

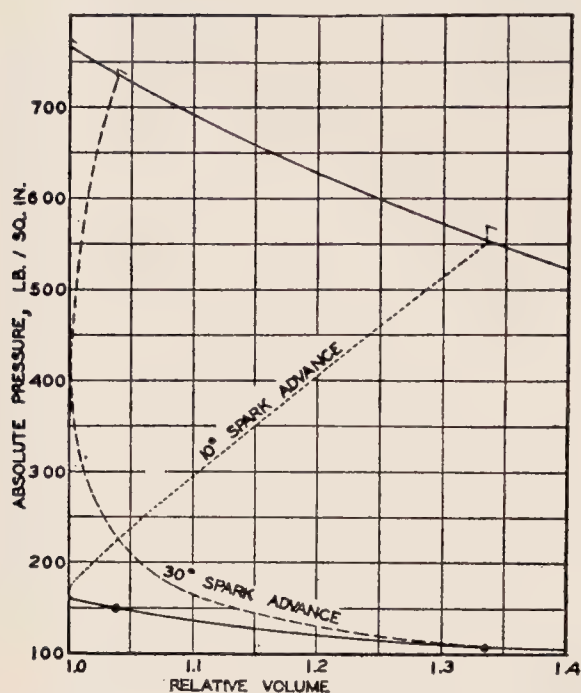


FIG. 10. High-pressure end of indicator card for conditions of Fig. 9. (Note: zero of P and maximum V not shown.)

bustion starts at a lower pressure than in the previous example. During the early stages of combustion the pressure rise is more rapid than in the previous example, by virtue of the combined effects of combustion and compression by the piston. Beyond top dead center, however, the expansion resulting from piston movement causes a decrease in the slope of the curves. This latter effect is particularly pronounced in the example with 10° spark advance, since nearly all the combustion occurs during the expansion stroke.

With the relation of pressure to fraction burned known, the calculation of the temperature distribution curves presented in the right half of Fig. 9 is as described in the first example. These curves show clearly the increase in temperature caused by advancing the spark. Of particular interest are the two lowermost curves, which represent the temperature in the unburned portion into which the flame is advancing. Near the end of combustion the temperature of the unburned gas is about 100° higher when the spark advance is 30° than when it is 10° . This temperature difference, alone or in conjunction with the large pressure difference occurring simultaneously, undoubtedly affects the nature of the reactions ahead of the flame front where "knock" probably starts. It is to be noted also that the usually calculated compression temperature is that at $c = 0$, which is several hundred degrees lower than the actual temperature in the later stages of combustion.

Experimental studies of the variation in flame temperature across an engine head confirm the general character of the upper curves of Fig. 9. Rassweiler and Withrow,¹⁶ using the sodium D line-reversal method to measure temperatures in an engine operating with open throttle with 80 per cent of theoretical air and a compression ratio of 4.4, found the temperature at the firing end to rise from 4200°R (at 10° of crank revolution after firing) to a peak of 4800°R , under nonknocking conditions. Calculations following the method of the present paper, with the simplifying assumption of all combustion occurring at top dead center, indicated temperatures at the spark plug of 4220°R and 5250°R at the start and completion of combustion, respectively. That the latter value is considerably in excess of that obtained by experiment is to be expected, since the time of combustion was not zero, but approximately 40° of crank revolution.

The relation of pressure to total chamber volume, for the three examples considered, was obtained by combining the V - c and p - c relations of Figs. 7 and 8. The results are presented in Fig. 10, which represents an enlargement of the upper corner of the calculated indicator cards for the three cases. The solid curve, part of which is the left edge, corresponds to combustion at top dead center. It is to be noted that the area of the card for 30° spark advance is only slightly less (about 2 per cent) than that of the conventionally "ideal" cycle; an important conclusion is that the simplification of calculations of the efficiency of various engine cycles by assuming combustion at top dead center, does not lead to any great error. The area of the indicator card for 10° spark advance, however, is much less than that of the others. According to Fig. 10 it is approximately 40,000 ft-lb or 51 Btu less than the "ideal" cycle. The latter cycle, according to the first example discussed, yields a work output of 463 Btu, from which one concludes that retarding the spark advance from 30° to 10° is accompanied by approximately 10 per cent loss in efficiency.

Summary

Quantitative calculations of the effects of flame propagation and of piston movement on the temperatures attained in the various parts of an Otto-cycle engine charge during combustion are made relatively simple by the use of a Mollier diagram of the properties of the combustion products of octane and air. The method is applied to a consideration of the effect of spark advance on the temperature attained ahead of the flame front, and it is concluded that the results are significant in studies of engine knock.

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INFLAMMATION LIMITS AND THEIR PRACTICAL APPLICATION IN HAZARDOUS INDUSTRIAL OPERATIONS*

G. W. JONES

Explosives Division, Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pennsylvania

Introduction

One of the major activities of the United States Bureau of Mines is the promotion of safety in mining and other industries. Investigations are carried out in connection with these activities to determine the explosion hazards of combustible gases, vapors, and solids and to investigate means of controlling and preventing explosions.

The limits of inflammability (explosive limits) of combustibles are not only of theoretical but also of great practical importance, because most industries, at one time or another, must contend with explosive mixtures of combustible gases or vapors in their manufacturing processes. The organic chemical industry has made rapid progress during the last twenty years, and numerous combustible liquids and gases which heretofore were either unknown or were mere laboratory curiosities are now manufactured in large quantities. The manufacture and marketing of these newer chemicals require a knowledge of the explosion hazards involved.

Combustible gases and vapors may be classed as one of the major hazards in present industrial operations, and there is need for a greater appreciation of the hazards involved in handling these gaseous mixtures and a better understanding of means of mitigating and preventing explosions.

Limits of Inflammability

Confusion has arisen regarding the meaning of the terms "explosive limits," "inflammation limits," and "limits of inflammability." These different expressions, in the final analysis, mean the same thing. Some authorities regard explosive limits as those limiting mixtures within which flame will propagate through the entire volume of the mixture and develop considerable pressure, while inflammation limits or limits of inflammability are regarded as those limiting mixtures within which flame will propagate through the mixture indefinitely, irrespective of whether or not pressure is developed.

It is impossible to distinguish an inflammation from an explosion by the amount of violence produced. Mixtures just within the limits of inflammability, if confined in a long tube and

tested by opening one end and igniting at this open end, will propagate flame quietly and slowly through the tube (usually at a uniform speed) and the speed, for a given concentration of combustibles in air, will vary with the direction of flame propagation. This same mixture, if confined in a closed bomb of sufficient size and ignited when the gases are in motion or gentle turbulence, will propagate flame at a speed many times as fast as that in the open tube and develop pressures ranging up to 30 lb or more per square inch. Thus the violence and pressure developed by an inflammable mixture depend upon the environment and direction of flame propagation; therefore no differentiation should, or can, be made between explosive limits and limits of inflammability.

1. *Factors Affecting the Limits of Inflammability.*

Only a brief discussion of the various factors affecting the limits of inflammability will be given. A more complete discussion is given in published reports.^{5,6,8} The limits are affected by the direction of flame propagation, the design, diameter, and length of the test apparatus, the temperature and pressure of the mixture at the time of ignition, the percentage of water vapor present, and indirectly by the source of ignition.

Wider limits are obtained for upward propagation of flame than for horizontal or downward propagation, therefore the risk of an explosion is greater when the mixtures are ignited from below than when ignited from above.

The limits of inflammability are widened as the diameter of the apparatus is increased, rapidly at first and then more slowly as the diameter approaches 2 in. Apparatus greater than 2 in. in diameter gives limit values very little different from those obtained with 2-in. apparatus.

The apparatus must be long enough to insure continued propagation of flame after the heat imparted to the mixture by the source of ignition has been dissipated. An apparatus 3 ft or more in length is sufficient.

It has been found that, if the apparatus is closed when the mixtures are ignited and ignition is initiated near the closed end when the gases are in gentle turbulence, the lower limit is reduced slightly.¹⁵

Ordinary variations of laboratory temperatures have no appreciable effect on the limits of inflammability. Elevated temperatures cause widening of the limits.

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Normal variations of atmospheric pressure have no appreciable effect on the limits. The effect of high pressures on the limits is neither simple nor uniform, but is specific for each inflammable mixture. As yet, no means has been developed for predicting the effect of high pressures on the limits of inflammability for any given combustible in air. In certain cases both limits are raised, in others the limits are narrowed, and in some both limits are changed as the pressure is increased.

The normal quantity of water vapor present in atmospheres at laboratory temperatures affects the lower limit of inflammability only to a slight extent. The presence of water vapor reduces the upper limit because some of the oxygen in the mixture is displaced by the water vapor, and, since the oxygen concentration is the important factor in an upper-limits mixture, as the oxygen is lowered the amount of combustible that can be burned is decreased, and so the limit is lowered.

2. *Limits of Inflammability of Gases and Vapors.*

Industrial safety requires that only values for the limits of inflammability of gases and vapors in air, which are obtained in apparatus giving the widest limits, be used. Keeping the above fact in mind, tabulations of the limits of inflammability of combustible gases and vapors have been made and are given in Tables I, II, and III. Values reported in the literature that were obtained in small apparatus and those in which the direction of flame propagation was other than upward have not been used, except where no other reported values were available. In some cases values reported by several investigators were found to be in good agreement; however, only one reference has been given.

The ratios between the amount of combustible in the limit mixtures and the amount of combustible required for theoretical complete combustion with air and the relationship between the amounts of combustible in the limit mixtures and their net heats of combustion are given.

Burgess and Wheeler³ first showed that there was a definite relationship between the calorific value of the combustible and its lower limit of inflammability; that is, the calorific values of the pure paraffin hydrocarbons times their lower limits of inflammability were a constant and that a lower-limit mixture of any of the paraffin hydrocarbons with air on combustion liberates the same amount of heat. Most of the "hot wire" combustible-gas indicators operate on this principle.

Some time later Thornton³⁴ announced that the upper limit bears a direct relation to the amount of oxygen needed for perfect combustion (theoretical complete combustion). He stated

that in the case of paraffins the upper limit contained twice as great a volume of gas as the mixture for perfect combustion, acetylene and carbon disulfide three times the volume, hydrogen four times, and carbon monoxide six times the volume. Lower-limit mixtures which just failed to propagate flame contained twice the volume of oxygen needed for perfect combustion in the case of the paraffins, and thrice the volume in the case of the other gases. The values given in Tables I, II, and III show that some of the predictions given by Thornton are approximately correct, while in other cases there are extremely wide variations, and that the classification is not nearly so simple as Thornton predicted.

The relationship between the calorific value of the combustibles, the oxygen required for perfect combustion, and the limits of inflammability was investigated and extended by White⁵¹ to cover a number of solvent vapors. He found that for all solvents examined, except one, the lower limit for downward propagation of flame was approximately inversely proportional to the net calorific value of the vapor used. The corresponding upper limit roughly followed a similar rule, it being about 3.5 times the lower limit. He also found that the amount of oxygen available for the combustion of a vapor in its limit mixture bore a fairly constant ratio to the amount required for the perfect combustion of 1 mole of the vapor. Thus the amount of solvent in a lower-limit mixture for downward propagation of flame was 0.57 of that present in the mixture for perfect combustion, while the ratio for the upper-limit mixture was just under 2.

The results given in Table IV show that no general relationship of the limits of combustible gases and vapors either to the amount of oxygen required for theoretical complete combustion or to the calorific value of the gases or vapors exists, nor do they give even approximately correct results if used indiscriminately.

On the other hand, if the combustibles are classified according to types of compounds the relationship between the limits and the oxygen required for theoretical complete combustion is of value in predicting the limits of inflammability of new compounds, the limits of which have not already been determined, as will be shown later.

3. *Calculation of Limits of Inflammability of Mixtures of Combustibles.*

The calculation of the limits of inflammability of combustible mixtures from a knowledge of the limits of each combustible in air and the percentages of each combustible present in the mixture can be done quite accurately for a great number of mixtures by the application of the so-called "mixture law."

Le Chatelier²⁸ first applied the law to the limits

TABLE I
Limits of inflammability of hydrocarbons in air

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Type	Name	Formula	Limits of inflammability, per cent by volume		Per cent combustible in air. Mix- ture for theoretical complete combustion	Ratio of lower limit to p.c.c.† = Col. 4 ÷ Col. 6	Ratio of upper limit to p.c.c. = Col. 5 ÷ Col. 6	Net heat of combustion, in kg.-cal. per mole	Lower limit × h.c.‡ = Col. 4 × Col. 9	Upper limit × h.c. = Col. 5 × Col. 9
			Lower	Upper						
Paraffin hydrocarbons	Methane	CH ₄	5.00 [15]§	15.00 [15]	9.47	0.53	1.58	191.7	958	2876
	Ethane	C ₂ H ₆	3.22 [8]	12.45[8]	5.64	0.57	2.21	336.7	1084	4192
	Propane	C ₃ H ₈	2.37[8]	9.50 [8]	4.02	0.59	2.36	484.1	1147	4599
	Butane	C ₄ H ₁₀	1.86 [8]	8.41 [8]	3.12	0.60	2.70	634.4	1180	5335
	Isobutane	C ₄ H ₁₀	1.80 [17]	8.44 [17]	3.12	0.58	2.71	630.6	1135	5322
	Pentane	C ₅ H ₁₂	1.40 [17]	7.80 [17]	2.55	0.55	3.06	774.9	1085	6044
	Isopentane	C ₅ H ₁₂	1.32 [3]		2.55	0.52		780.1	1030	
	Hexane	C ₆ H ₁₄	1.25 [17]	6.90 [17]	2.16	0.58	3.19	915.9	1145	6320
	Heptane	C ₇ H ₁₆	1.00 [31]	6.00 [31]	1.87	0.53	3.21	1064.5	1065	6387
	Octane	C ₈ H ₁₈	0.95 [17]		1.65	0.58		1207.7	1147	
	Nonane	C ₉ H ₂₀	0.83 [28]		1.47	0.56		1353.0*	1123	
	Decane	C ₁₀ H ₂₂	0.67 [31]		1.33	0.50		1494.0	1001	
Olefins	Ethylene	C ₂ H ₄	2.75 [26]	28.60 [26]	6.52	0.42	4.39	310.9	855	8892
	Propylene	C ₃ H ₆	2.00 [17]	11.10 [17]	4.44	0.45	2.50	460.5	921	5112
	Butylene	C ₄ H ₈	1.70 [36]	9.00 [36]	3.37	0.50	2.67	611.7	1040	5505
	Amylene	C ₅ H ₁₀	1.60 [29]		2.71	0.59		750.6	1201	

Acetylenes	Acetylene	C_2H_2	2.50 [17]	80.00 [36]	7.72	0.32	10.36	301.5	754	24120
Aromatics	Benzene	C_6H_6	1.41 [17]	6.75 [17]	2.71	0.52	2.49	750.6	1058	5067
	Toluene	C_7H_8	1.27 [13]	6.75 [37]	2.27	0.56	2.97	892.0	1133	6021
	<i>o</i> -Xylene	C_8H_{10}	1.00 [31]	6.00 [31]	1.95	0.51	3.08	1038.9	1039	6233
Cyclic hydrocarbons	Cyclopropane	C_3H_6	2.40 [17]	10.40 [17]	4.44	0.54	2.34	465.1	1116	4837
	Cyclohexane	C_6H_{12}	1.33 [2]	8.35 [2]	2.27	0.59	3.68	875.6	1165	7311
	Methylcyclohexane	C_7H_{14}	1.15 [30]		1.95	0.59		1017.9	1171	
Terpenes	Turpentine	$C_{10}H_{16}$	0.80 [31]		1.47	0.55		1385.5	1108	

* Estimated.

† p.c.c. = per cent combustible in air. Mixture for theoretical complete combustion.

‡ h.c. = net heat of combustion.

§ Numbers in brackets are reference numbers

TABLE II
Limits of inflammability of alcohols, aldehydes, ethers, ketones, acids, and esters in air

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	
Type	Name	Formula	Limits of inflammability, per cent by volume		Per cent combustible in air. Mix- ture for theoretical complete combustion	Ratio of lower limit to p.c.c.† = Col. 4 ÷ Col. 6	Ratio of upper limit to p.c.c. = Col. 5 ÷ Col. 6	Net heat of combustion, in kg.-cal. per mole	Lower limit × h.c.‡ = Col. 4 × Col. 9	Upper limit × h.c. = Col. 5 × Col. 9	
			Lower								Upper
Alcohols	Methyl alcohol	C ₂ H ₆ O	6.72 [22]§	36.50 [37]	12.24	0.55	2.98	149.8	1007	5468	
	Ethyl alcohol	C ₂ H ₆ O	3.28 [13]	18.95 [38]	6.52	0.50	2.91	295.9	971	5607	
	Propyl alcohol	C ₃ H ₈ O	2.55 [28]		4.44	0.57		438.3	1118		
	Isopropyl alcohol	C ₃ H ₈ O	2.65 [28]		4.44	0.60		432.6	1146		
	Butyl alcohol	C ₄ H ₁₀ O	1.70 [31]		3.37	0.50		585.8	996		
	Isobutyl alcohol	C ₄ H ₁₀ O	1.68 [28]		3.37	0.50		585.4	983		
	Amyl alcohol	C ₅ H ₁₂ O	1.19 [28]		2.71	0.44		730.3	869		
	Isoamyl alcohol	C ₅ H ₁₂ O	1.20 [31]		2.71	0.44		711.6	854		
	Allyl alcohol	C ₃ H ₆ O	2.40 [31]		4.97	0.48		410.6	985		
Aldehydes	Acetaldehyde	C ₂ H ₄ O	3.97 [37]	57.00 [37]	7.72	0.51	7.38	257.8	1023	14695	
	Crotonaldehyde	C ₄ H ₆ O	2.12 [22]	15.50 [17]	4.02	0.53	3.86	510.4	1082	7911	
	Furfural	C ₅ H ₄ O ₂	2.10 [21]		4.02	0.52		538.4	1131		
	Paraldehyde	C ₆ H ₁₂ O ₃	1.30 [31]		2.71	0.48		788.1*	1025		
Ethers	Methyl ethyl ether	C ₃ H ₈ O	2.00 [31]	10.10 [31]	4.44	0.45	2.27	461.1	922	4657	
	Diethyl ether	C ₄ H ₁₀ O	1.85 [26]	36.50 [26]	3.37	0.55	10.83	598.8	1108	21856	
	Divinyl ether	C ₄ H ₆ O	1.70 [14]	27.60 [14]	4.02	0.42	6.72	569.1	967	15366	

Ketones	Acetone	C_3H_6O	2.55 [15]	12.80 [15]	4.97	0.51	2.58	395.0	1007	5056
	Methyl ethyl ketone	C_4H_8O	1.81 [17]	9.50 [17]	3.67	0.49	2.59	540.1	978	5131
	Methyl propyl ketone	$C_5H_{10}O$	1.55 [17]	8.15 [17]	2.90	0.53	2.81	682.8	1058	5565
	Methyl butyl ketone	$C_6H_{12}O$	1.22 [17]	8.00 [17]	2.40	0.51	3.33	831.8	1015	6654
Acids	Acetic acid	$C_2H_4O_2$	4.05 [29]		9.47	0.43		188.3	763	
	Hydrocyanic acid	HCN	5.60 [32]	40.00 [32]	14.34	0.39	2.79	154.4	865	6176
Esters	Methyl formate	$C_2H_4O_2$	5.05 [23]	22.70 [23]	9.47	0.53	2.40	212.0	1071	4812
	Ethyl formate	$C_3H_6O_2$	2.75 [22]	16.40 [35]	5.64	0.49	2.91	359.9	990	5902
	Methyl acetate	$C_3H_6O_2$	3.15 [22]	15.60 [22]	5.64	0.56	2.77	349.4	1101	5451
	Ethyl acetate	$C_4H_8O_2$	2.18 [13]	11.40 [37]	4.02	0.54	2.84	494.7	1078	5640
	Propyl acetate	$C_5H_{10}O_2$	2.05 [2]		3.12	0.66		633.0*	1298	
	Isopropyl acetate	$C_5H_{10}O_2$	2.00 [33]		3.12	0.64		638.0	1276	
	Butyl acetate	$C_6H_{12}O_2$	1.70 [2]		2.55	0.67		768.4	1306	
	Amyl acetate	$C_7H_{14}O_2$	1.10 [31]		2.16	0.51		968.6	1065	

* Estimated.

† p.c.c. = per cent combustible in air. Mixture for theoretical complete combustion.

‡ h.c. = net heat of combustion.

§ Numbers in brackets are reference numbers.

TABLE III
Limits of inflammability of miscellaneous combustible gases and vapors in air

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Type	Name	Formula	Limits of inflammability, per cent by volume		Per cent combustible in air. Mix- ture for theoretical complete combustion	Ratio of lower limit to p.c.c.† = Col. 4 ÷ Col. 6	Ratio of upper limit to p.c.c. = Col. 5 ÷ Col. 6	Net heat of combustion, in kg.-cal. per mole	Lower limit × h.c.‡ = Col. 4 × Col. 9	Upper limit × h.c. = Col. 5 × Col. 9
			Lower	Upper						
Hydrogen	Hydrogen	H ₂	4.00 [11]§	74.20 [4]	29.50	0.14	2.52	57.8	231	4289
Carbon monoxide	Carbon monoxide	CO	12.50 [5]	74.20 [4]	29.50	0.42	2.52	67.6	845	5016
Nitrogen compounds	Ammonia	NH ₃	15.50 [9]	27.00*	21.82	0.71	1.24	76.2	1181	2057
	Cyanogen	C ₂ N ₂	6.60 [1]	42.60 [1]	9.47	0.70	4.50	258.3	1705	11004
	Pyridine	C ₅ H ₅ N	1.81 [37]	12.40 [37]	3.24	0.56	3.83	652.1	1180	8086
	Ethyl nitrate	C ₂ H ₅ NO ₃	3.80 [28]		10.68	0.36		296.0	1125	
	Ethyl nitrite	C ₂ H ₅ NO ₂	3.01 [37]	50.00 [37]	8.51	0.35	5.88	306.2	922	15310
Oxides	Ethylene oxide	C ₂ H ₄ O	3.00 [18]	80.00 [18]	7.72	0.39	10.36	281.0	843	22480
	Propylene oxide	C ₃ H ₆ O	2.00 [27]	22.00 [27]	4.97	0.40	4.43			
	Dioxan oxide	C ₄ H ₈ O ₂	1.97 [24]	22.25 [24]	4.02	0.49	5.53	539.8	1063	12011
	Diethyl peroxide	C ₄ H ₁₀ O ₂	2.34 [38]		3.67	0.64				
Sulfides	Carbon disulfide	CS ₂	1.25 [17]	50.00 [37]	6.52	0.19	7.67	246.6	308	12330
	Hydrogen sulfide	H ₂ S	4.30 [36]	45.50 [36]	12.24	0.35	3.72	122.5	527	5574
	Carbon oxysulfide	COS	11.90 [10]	28.50 [10]	12.24	0.97	2.33	130.5	1533	3719
Chlorides	Methyl chloride	CH ₃ Cl	8.25 [12]	18.70 [12]	12.24	0.67	1.53	153.7	1268	2874
	Vinyl chloride	C ₂ H ₃ Cl	4.00 [17]	21.70 [17]	7.72	0.52	2.81	270.9	1084	5879
	Ethyl chloride	C ₂ H ₅ Cl	4.00 [12]	14.80 [12]	6.52	0.61	2.27	295.6	1182	4375

Chlorides	Amyl chloride	$C_5H_{11}Cl$	1.40 [17]	2.71	0.52	731.9	1025
	Dichloroethylene	$C_2H_2Cl_2$	9.70 [7]	9.47	1.02	224.5	2178
	Ethylene dichloride	$C_2H_4Cl_2$	6.20 [19]	7.72	0.80	249.9	1549
	Propylene dichloride	$C_3H_6Cl_2$	3.40 [25]	4.97	0.68	396.1	1347
Bromides	Methyl bromide	CH_3Br	13.50 [12]	12.24	1.10	173.5	2342
	Ethyl bromide	C_2H_5Br	6.75 [12]	6.52	1.04	319.4	2156

* Average of several reported values.

† p.c.c. = per cent combustible in air. Mixture for theoretical complete combustion.

‡ h.c. = net heat of combustion.

§ Numbers in brackets are reference numbers.

TABLE IV

Limits of inflammability of selected gases and vapors in air showing variation of ratios between the percentage of combustibles in the limit mixtures and that required for theoretical complete combustion and the relationship between the limits and net heats of combustion

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Combustible	Formula	Limits of inflammability, per cent by volume		Per cent combustible in air. Mixture for theoretical complete combustion	Ratio of lower limit to p.c.c.* = Col. 3 ÷ Col. 5	Ratio of upper limit to p.c.c. = Col. 4 ÷ Col. 5	Net heat of combustion, in kg.-cal. per mole	Lower limit × h.c.† = Col. 3 × Col. 8	Upper limit × h.c. = Col. 4 × Col. 8
		Lower	Upper						
Hydrogen	H ₂	4.00	74.20	29.50	0.14	2.52	57.8	231	4289
Carbon disulfide	CS ₂	1.25	50.00	6.52	0.19	7.67	246.6	308	12330
Acetylene	C ₂ H ₂	2.50	80.00	7.72	0.32	10.36	301.5	754	24120
Hydrogen sulfide	H ₂ S	4.30	45.50	12.24	0.35	3.72	122.5	527	5574
Ethylene oxide	C ₂ H ₄ O	3.00	80.00	7.72	0.39	10.36	281.0	843	22480
Ethylene	C ₂ H ₄	2.75	28.60	6.52	0.42	4.39	310.9	855	8892
Methane	CH ₄	5.00	15.00	9.47	0.53	1.58	191.7	958	2876
Methyl alcohol	CH ₄ O	6.72	36.50	12.24	0.55	2.98	149.8	1007	5468
Methyl acetate	C ₃ H ₆ O ₂	3.15	15.60	5.64	0.56	2.77	349.4	1101	5451
Methyl chloride	CH ₃ Cl	8.25	18.70	12.24	0.67	1.53	153.7	1268	2874
Methyl bromide	CH ₃ Br	13.50	14.50	12.24	1.10	1.18	173.5	2342	2516

* p.c.c. = per cent combustible in air. Mixture for theoretical complete combustion.

† h.c. = net heat of combustion.

of inflammability of gases. The law states that if we have, say, separate limit combustible-air mixtures and mix them, then this mixture will also be a limit mixture. The equation for expressing this law in its simplest form is written as follows:

$$L = \frac{100}{(P_1/N_1) + (P_2/N_2) + (P_3/N_3) + (P_4/N_4)},$$

where P_1 , P_2 , P_3 , and P_4 are the proportions of each combustible gas present in the original mixture, free from air and inerts, so that $P_1 + P_2 + P_3 + P_4 = 100$, and N_1 , N_2 , N_3 , and N_4 are the lower limits of inflammability of each combustible in air.

As an example of the application of this law we may take a natural gas of the following composition:

Hydrocarbon present	Per cent by volume	Lower limit
Methane	80.0	5.00
Ethane	15.0	3.22
Propane	4.0	2.37
Butane	1.0	1.86

$$\begin{aligned} \text{Lower limit} &= \frac{100}{\frac{80.0}{5.00} + \frac{15.0}{3.22} + \frac{4.0}{2.37} + \frac{1.0}{1.86}} \\ &= 4.37. \end{aligned}$$

This law has been tested by Coward, Carpenter, and Payman⁵ and proved to hold for hydrogen, carbon monoxide, and methane containing no inert gases in normal air. Subsequent tests made with paraffin hydrocarbons in air⁸ showed that the law could also be applied to these mixtures. Exceptions have been found in tests made with some inflammable gases. White³⁷ found that the law does not hold strictly for hydrogen-ethylene-air mixtures, acetylene-hydrogen-air mixtures, hydrogen sulfide-methane-air mixtures, and mixtures containing carbon disulfide. Also, in tests on some chlorinated hydrocarbons, Coward and Jones⁷ found that the law did not hold for methane-dichlorethylene-air mixtures, and more recently it was found¹² that the law was only approximately correct for mixtures of methyl and ethyl chlorides. It is therefore apparent that the mixture law, useful when its application has been proved, cannot be applied indiscriminately, but must first be proved to hold for the gases being investigated.

Many industrial processes require the use of

mixtures of various solvents in their processes, and although the limits of inflammability of the various individual constituents in the mixture may be known, it is not at all certain what the inflammability limits will be for the various mixtures. Investigations of the lower limits of inflammability of solvent mixtures have shown that where the ratios of the lower limits of the individual constituents to the amount of oxygen required for theoretical perfect combustion are about the same, the limits of mixtures of the constituents may be determined accurately by calculation. For example, the limits of mixtures of ethyl alcohol, benzene, furfural, and acetone in which the ratios range from 0.50 to 0.53 (Tables I, II, and III) may be calculated, and mixtures of ethyl acetate, ethyl alcohol, and toluene, whose ratios vary from 0.50 to 0.56, have been found also to give calculated results agreeing closely with experimental results.¹³

At the present time, the accuracy of the above prediction has been proved only for a limited number of mixtures; however, as information on the subject is accumulated, the classification of compounds according to the ratios should be of great value in predicting and calculating the limits of inflammability of mixtures of combustible gases and vapors.

As an example to show the application of this method for predicting the limits of inflammability of combustibles whose limits have not been determined, propyl chloride may be used. The ratio of the lower limit of certain gases to that for theoretical complete combustion is as follows:

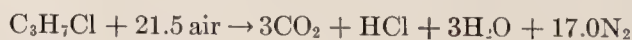
methane	0.52
ethane	0.57
propane	0.59
methyl chloride	0.67
ethyl chloride	0.61
propyl chloride	not known

The addition of one chlorine atom to methane has raised the ratio 0.15, while the addition of one chlorine atom to ethane has raised the ratio only 0.04. One chlorine atom added to propane should raise the ratio even less, say 0.02, thus giving a ratio of 0.61 for propyl chloride.

When propyl chloride is burned with the theoretical amount of oxygen to give complete combustion, the following reaction takes place:



or with air



The percentage of propyl chloride in a mixture with air to give theoretical complete combustion = $(1 \times 100)/22.5 = 4.44$ per cent. Using

the ratio 0.61 for propyl chloride given above, the predicted lower limit of inflammability = $4.44 \times 0.61 = 2.71$ per cent.

4. *Limits of Inflammability of Complex Mixtures.* It is possible to calculate closely the limits of inflammability not only of certain mixtures of combustible gases and vapors in air but also of mixtures containing varying amounts of inert gases. The limits of inflammability of natural, manufactured, producer, blast furnace, automobile, and sewage gases may be calculated from a knowledge of the composition of constituents composing the gases and their limits of inflammability. The actual procedure is rather long and complicated, so only a reference to this method will be given in this report.^{6,11,20,40}

Practical Means of Eliminating or Minimizing Explosions in Industrial Operations

1. Control of the Oxygen Content of the Atmosphere.

The fact that all combustible gases, vapors, mists, and pulverized solids will not burn or explode when the oxygen content is reduced below certain definite values, varying with the combustible materials under consideration, gives the safety engineer a means of definitely controlling and eliminating explosions.

The oxygen present in an explosive mixture may be reduced by direct absorption by means of special reagents, by dilution with inert gases such as nitrogen or carbon dioxide, or by combinations of these inert gases as represented by flue gas or exhaust gas from an internal-combustion engine. Flue gases made by burning fuel gas or fuel oil with the proper proportions of air and automobile exhaust gas both have a low oxygen content and are ideally suited for reducing the oxygen content of atmospheres. Carbon dioxide compressed in

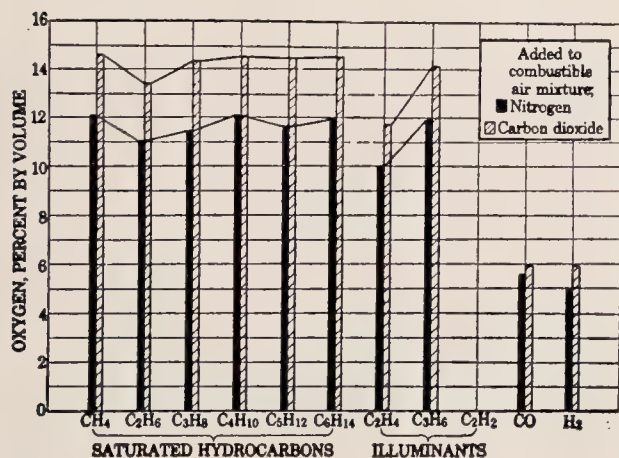


FIG. 1. Per cent oxygen by volume in gas mixtures below which explosions are prevented at ordinary temperatures and pressures.

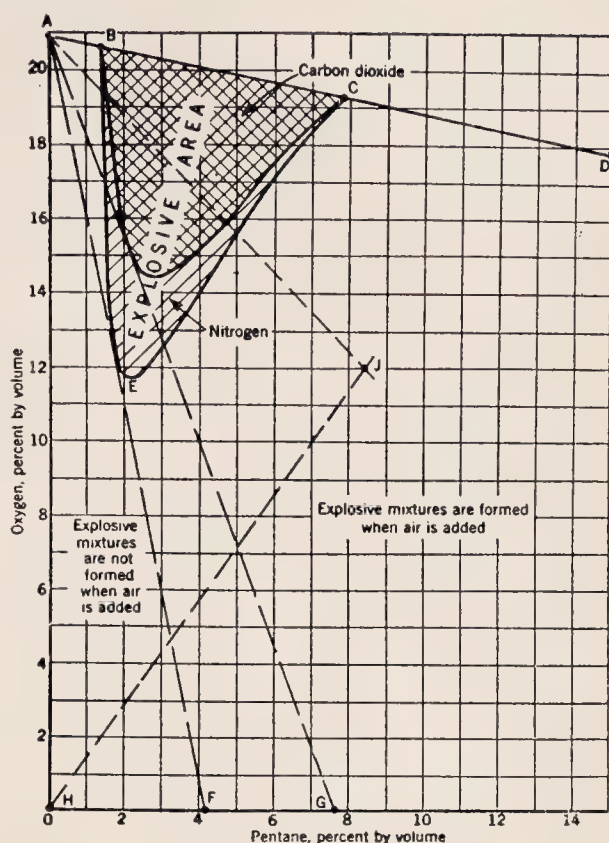


FIG. 2. Explosibility of mixtures of pentane, air, added nitrogen, and carbon dioxide.

cylinders, carbon tetrachloride, and dichlorodifluoromethane have been used also for this purpose.

The critical oxygen values below which flames will not propagate or explosions take place when the reduction of the oxygen content of the atmosphere is brought about by the addition of nitrogen and carbon dioxide for several hydrocarbons are shown graphically in Fig. 1. The critical oxygen value for any given combustible varies with the concentration of the combustible present; however, the values given in Fig. 1 are minimum ones and cover all concentrations of the combustible that might be present. The relationship between concentration of combustible and the critical oxygen requirements to prevent explosions is shown to better advantage in Fig. 2. This graph shows the explosive areas of all possible mixtures of pentane, air, and added nitrogen or carbon dioxide. The straight line *AD* represents the composition of mixtures of pentane and pure air containing up to 15 per cent pentane. The limits as shown on this line are seen to be 1.4 per cent for the lower and 7.8 per cent for the upper limit. All mixtures between these limits are explosive. As nitrogen or carbon dioxide is added the oxygen concentration is lowered and, as shown, the limits are narrowed. Finally when the oxygen content is reduced to 11.7 per cent

all mixtures of pentane, air, and added nitrogen become non-explosive. The mixture which will propagate flame with a minimum concentration of oxygen contains 2.10 per cent of pentane. If the atmosphere contains 5.00 per cent of pentane the graph shows that the oxygen concentration needs to be reduced to only 15.6 per cent. Although this mixture having 5.00 per cent of pentane will not explode when the oxygen content is below 15.6 per cent, the graph shows that if air is added to the mixture it becomes explosive, since addition of air shifts the composition of the mixture along the line to the left and towards the *A*-axis, so that the composition passes through a range of mixtures which are explosive.

The usual problem in dealing with pentane-air mixtures is to control the atmosphere so that the composition at all times is outside the explosive area bounded by *BCE* (when added nitrogen is used as the diluent). A graph of this type enables one to determine at a glance the explosive hazards involved. If an analysis is made of an atmosphere and it is found to contain, say, 12 per cent oxygen and 8.40 per cent pentane, this mixture, as indicated by the point *J* on the graph, shows at once that the mixture cannot explode until air is added; however, if the equipment is to be taken out of service and it is desired to do so without possibility of explosions, the atmosphere must be altered so as to pass around the explosive area. It becomes necessary to alter the composition of the atmosphere until it falls into the area to the left of the line *AEF*, and in no case should it fall into the explosive area indicated. It is not necessary to reduce the oxygen content to zero to pass safely from the composition given by point *J* to atmospheres of the composition given by any point to the left of the line *AEF*. Nitrogen can be added until the oxygen content is reduced to below 4.6 per cent, thus shifting the composition along the line *JH* and reducing the pentane content to a value of 3.3 per cent or less, until it passes into the area to the left of the line *AEF*. The composition of the atmosphere now is such that it cannot be made explosive, no matter how much air is added, because a line drawn from any point in this area to *A* will not pass through the explosive area. Air can then be added to the equipment and the combustibles swept out without any danger of explosions. The graph given holds only for pentane, and graphs of a similar type must be constructed for each hydrocarbon concerned.

2. *Carrying Out Operations so that the Percentages of Combustibles Present are Outside the Limits of Inflammability.* Processes that necessitate the use of combustible gases or vapors should be carried out wherever possible under conditions

in which the atmospheres are outside the limits of inflammability of the materials used. If possible, the concentrations should be kept below the lower limit of inflammability, because under these conditions if air finds its way into the mixture, there is no danger of explosions. If the concentration of combustibles must be above the lower limit of inflammability, then it is advisable to raise the concentration until the combustibles present are above the upper limit. No explosion hazards will result while the atmospheres are above the upper limit; the danger arises when additional air finds its way into the mixture, and this usually occurs when the process is started up or closed down.

If combustible liquids are used the explosion hazards may be controlled by regulation of the temperature, and in turn the vapor pressures should be so regulated that the atmosphere is either above or below the limits of inflammability. In the application of this method of control the limits of inflammability of the vapor in air and the vapor pressures of the material over the temperature range to be used must be known. The application of this method to a gasoline is given in Fig. 3. The lower limit of inflammability of the gasoline in air is 1.40 and the upper limit 6.90 per cent of volume; then at 1 atm of pressure the gasoline must have a vapor pressure of 10.5 mm of mercury to give a lower-limit and 52.5 mm to give an upper-limit mixture. The two horizontal lines enclose the limits within which inflammable mixtures are produced, and the intersections of these lines with the vapor pressure curve give the range of vapor pressure that can produce inflammable mixtures. The corresponding temperatures in this particular case are 4°F and 77°F. The graph shows that this gasoline should be used at temperatures either below 4°F or above 77°F, if the process is to be

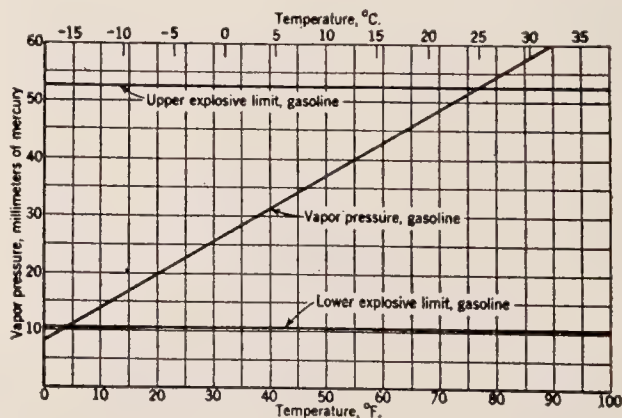


FIG. 3. Relationship between limits of inflammability and vapor pressure of a combustible liquid.

carried out under conditions where explosive mixtures will not be present.

If combustible liquids or mixtures of which the vapor pressures are not known are used in a process, the temperature range over which explosive mixtures may be present may be easily determined by means of the simple apparatus shown in Fig. 4. Explosion tube D is 2.5 cm (1. in) in diameter and 20 cm (8 in.) long. E indicates the electrodes across which sparks generated from a transformer M and induction coil N are passed when a test of the explosibility of the atmosphere in tube D is desired. H and H' are mercury seals through which contact is made between the electrodes and the induction coil N. The explosion tube D is immersed in a liquid bath, C, kept at uniform temperature by stirrer L, and heated to the desired temperature by burner O. K is a thermometer for recording the temperature of the bath.

To determine the temperature range over which a combustible liquid gives explosive mixtures, the combustible liquid is poured into D until the level is about 2 cm (0.8 in.) below the electrodes, and a cork R, having an opening as shown, is placed in the top of explosion tube D. Air is turned on and adjusted to give at the start three bubbles per second, as indicated by bubbler A. The air is then passed through tower B containing a drying agent, and thence through the glass coil G in the bath to bring the air to the temperature of the bath before it enters the combustible liquid F in explosion tube D. Air is passed through the liquid at the rate given for 5 min at a given temperature, and a test for explosibility is made by removing cork R and causing sparks to pass at the electrodes (E). If the combustible liquid gives an explosive mixture with air at the temperature tested, flame will pass up the tube and out the top. Tests are continued by the method of trial and error until a minimum temperature is obtained at which flame carries from the electrodes upward through

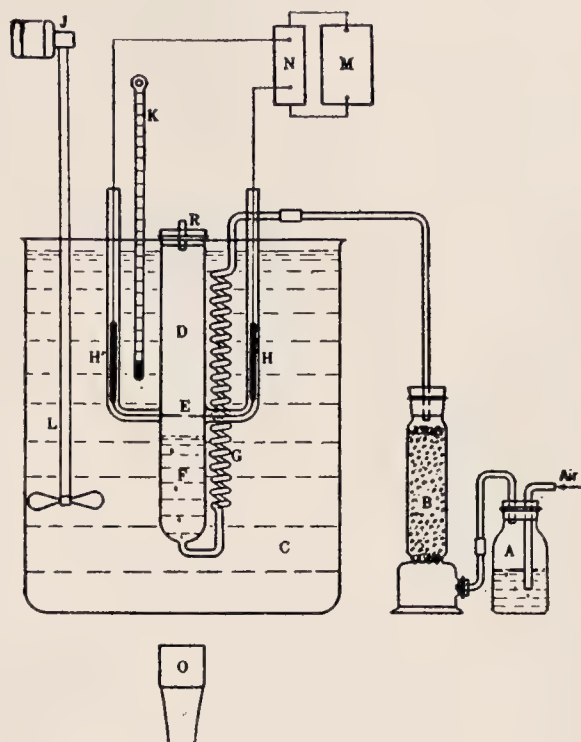


FIG. 4. Apparatus for determining the explosive range of high-boiling hydrocarbons.

the tube. The temperature is then kept constant and the rate of air flow changed until a rate is found which gives the lowest temperature that causes inflammation of the mixture in the tube. The temperature of the bath is then raised and the temperature at the upper-limit mixtures is ascertained in a similar manner.

The limits of inflammability of combustible liquids may be determined rather closely in the apparatus described, provided the vapor pressures of the liquids tested are accurately known. To obtain the limits, the vapor pressure of the liquid at the temperature at which flame is propagated is divided by the barometric pressure at the time of the experiment and multiplied by 100. Tests made both in the apparatus described

TABLE V

Effect of substitution of chlorine atoms for hydrogen upon the explosibility of methane

Substance	Formula	Explosibility	Limits of inflammability, per cent by volume	
			Lower	Upper
Methane	CH ₄	Highly explosive with air	5.00	15.00
Methyl chloride	CH ₃ Cl	Moderately explosive with air	8.20	18.70
Methylene chloride	CH ₂ Cl ₂	Not explosive with air	No explosive limits	
Chloroform	CHCl ₃	Not explosive with air	No explosive limits	

and in large-scale apparatus have shown approximate agreement.

3. *The Use of Less Inflammable Combustibles.* Wherever possible, solvents or other materials with the least inflammable characteristics should be used. Those materials should be chosen which have, at the temperatures used, vapor pressures that give atmospheres that are not explosive. When this cannot be done the use of chlorinated hydrocarbons should be considered. Table V shows how a combustible gas which has one or more hydrogen atoms replaced by chlorine gives resulting materials with reduced explosive characteristics.

Methane becomes highly explosive when mixed with the proper proportions of air. While methyl chloride does not produce as violent explosions as methane-air mixtures, nevertheless explosions of this substance in air may do considerable damage. Methylene chloride is entirely safe when mixed with air at ordinary temperatures and pressures; however, when mixed with pure oxygen in the right proportions, it becomes highly explosive. Chloroform has no explosive properties. Carbon tetrachloride is entirely nonexplosive with air in any proportions, and is used to good advantage in the preparation of noncombustible and nonexplosive safety cleaning compounds when added in the proper proportions to combustible liquids such as naphtha and petroleum distillates.

4. *Elimination of Ignition Sources.* Combustible gases and vapors, mixed with air or pure oxygen in the proportions to give explosive mixtures, may be safely used provided all sources of ignition are eliminated. Before a mixture can be made to explode, a portion of it must be heated to its ignition temperature. The ignition temperature may be defined as that temperature at which rapid combustion becomes independent of external supplies of heat.

It is not the purpose of this report to discuss ignition temperatures other than to state briefly that values reported in the literature are variable, can be used only in a relative sense, and may be even misleading unless complete details of the procedure by which the results were obtained are given. The results obtained depend upon and are affected by a number of variables, the most important of which are the percentage of combustible in the mixture, the oxygen concentration, the "lag" or time required at a given temperature to cause ignition, the size, composition, and dimensions of the equipment in which the tests are made, the pressure at which the mixture is confined at the time of ignition, and the presence of catalysts and impurities in the mixtures.

The safety engineer is primarily interested in the sources of ignition that may cause explosions. These sources may be represented by the classification given below:

IGNITION SOURCES:

FLAMES:

- Open lights
- Matches and cigarette lighters
- Fires in boilers; water heaters
- Burning material; incinerators

SPARKS:

- Static electricity
- Electrical shorts
- Lightning
- Sparks from tools

HEATED MATERIALS:

- Glowing metals, cinders, and filaments
- Electric lights

Most of the sources of ignition given above can be taken care of by establishing proper safety regulations and installing flame-proof electrical equipment; others by designing the plants so that boilers, water heaters, and other equipment where there are open flames and incandescent materials are installed in other buildings at a safe distance from the place where the hazardous processes are carried out.

Static electricity has caused many serious fires and explosions and is one of the most serious ignition hazards to control. There are few operations in which it may not be present, and it is more serious in dry atmospheres when the relative humidity is below 60 per cent. Static is generated by friction, that is, by slipping belts, pulleys, and revolving machinery and by the passage of solids, liquids, or gases at high velocity through small openings.

Static electricity may be eliminated by grounding all machinery, pipes, and other equipment where charges may accumulate. To accomplish this, permanent metallic conductors should be connected to the pipes of the water system. In the case of moving equipment, metallic collectors or "combs" should contact the moving parts and so ground the charges that may collect on the equipment.

5. *Segregation of Hazardous Operations.* Operations which through necessity rather than choice require the use of inflammable gases or vapors should be segregated from other operations. This requires the installation of hazardous processes in buildings at a safe distance from others and, if heavy combustible vapors are used, the elevation should be below that of other buildings so that in case of a fire or explosion the liquids and vapor that may be released will not flow toward other adjacent buildings. A hill or

artificial earth barrier should be constructed where the operations are exceedingly dangerous.

6. *The Provision of Adequate Ventilation.* The necessity for adequate ventilation in buildings cannot be too strongly emphasized where inflammable gases and vapors are handled and used. This includes not only the buildings in which the vapors are used but also all conduits, trenches, and tunnels where lines for conveying inflammable gases and vapors, and pipe lines for conveying inflammable liquids, are installed. Such lines should be carried in the open air above ground from one building to another, and in buildings they should be suspended above the floor level where they can be inspected readily for leaks.

Buildings should be made of light material which will offer not too great a resistance to pressure if an explosion occurs. The top should be provided with open ventilators, and windows should be installed in sashes of the tilting type which open when pressure is exerted from the inside.

It is impossible to have too much ventilation around hazardous operations. Where possible the operations should be carried out entirely in the open air, with no buildings whatever except those to house recording and other delicate instruments.

7. *Construction of Smooth Fireproof Floors.* Smooth, fireproof floors resistant to the penetration of liquid combustibles should be used in buildings where hazardous operations are carried out. The floors should be laid directly on an earth foundation with no unventilated spaces under-

neath. They should be cleaned and scoured periodically. Many disastrous fires have been due to oils, greases, and hydrocarbon deposits being allowed to accumulate on the floors. Although such deposits are normally safe from explosion hazards, they may become exceedingly hazardous if a small fire or explosion develops in the plant, since because of the resulting high temperature the deposits vaporize and burn and are very difficult to extinguish when once set on fire.

8. *Release Diaphragm.* Adequate light-weight release diaphragms should be provided on all equipment in which explosive mixtures may be present. The ideal release diaphragm is that having zero mass and an infinite area. This cannot be realized in practice; however, the construction and size of release openings should approach the above ideal as closely as possible, yet be of sufficient strength to sustain the operating pressure within the equipment without danger of rupture or leakage except in the case of an explosion within the equipment.

To protect properly a given installation containing explosive mixtures, the following factors must be known or determined experimentally. (1) The type and concentration of explosive mixtures that may be present in the equipment. (2) The maximum pressure the equipment will safely stand. (3) The area of release openings necessary to keep the pressures below the safe maximum pressure. (4) The type of diaphragm material that will rupture at the desired pressures. (5) The location of the release diaphragms so that there will be no unprotected dead ends. Space does not permit a complete discussion of

TABLE VI

Pressures developed by explosive mixtures of acetone-air with varying sizes of release openings, in pounds per square inch above atmospheric pressure in 8-liter bomb

Acetone, per cent by volume	Round hole, diameter of opening, in.							Square hole, width, in.	
	Closed	0.25	0.50	1.00	2.00	3.00	4.00	1.5	2.5
3.00	36	17.0	7.0	2.0	0.5	0.5	0.5	0.5	0.5
4.00	61	40.0	20.0	7.0	2.5	0.5	0.5	2.5	0.5
5.00	74	65.0	45.0	12.0	4.0	1.5	0.5	5.0	1.5
5.50	78		49.0	14.0	4.5	2.0	0.5	6.0	2.0
Ratio = (volume in cu ft)/(area opening in sq in.)	Infinite	5.79	1.446	0.362	0.0905	0.0402	0.0226	0.126	0.0454
Area of opening in sq. in. per cu. ft	0.00	0.17	0.69	2.77	11.05	24.90	44.30	7.9	22.0

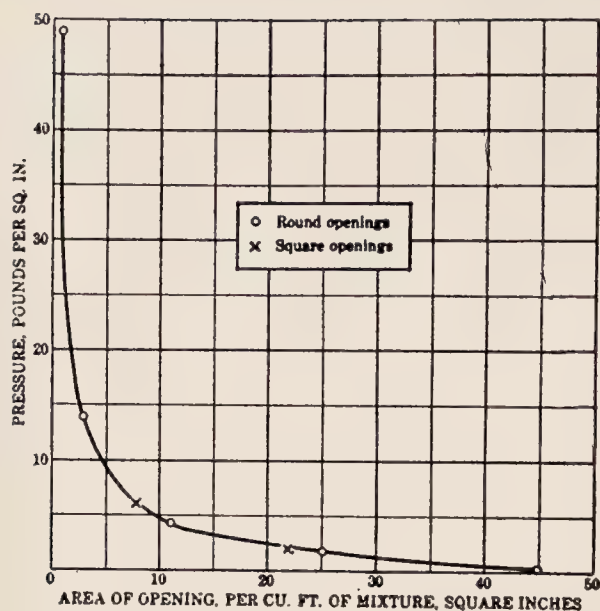


FIG. 5. Curve of relation of pressures produced to area of opening, 5.50 per cent acetone-air mixtures. 8.05-liter bomb.

these factors, so only one example will be given to show how the proper diaphragm releases may be determined.

The pressures developed when mixtures of acetone and air of varying concentration are ignited in the bomb provided with different release openings are given in Table VI. The results show that the maximum pressure developed in the bomb occurs when the concentration of acetone equals about 5.5 per cent by volume. Using the values giving the maximum pressure development for the various-size release openings tested, the curve shown in Fig. 5 is obtained. This gives the pressure developed when the area of release openings is varied from

zero opening to 45 sq. in. per cubic foot of space in the equipment. Assume that the equipment should not be subjected to a pressure greater than 10 psi, then the area of release openings should be approximately 5 in.²/ft³ of space.

The next important factor is the determination of the proper size, material, and thickness of the diaphragm material which will provide release of the gases from the equipment at a pressure of 10 lb or less. In general, lead, tin, aluminum, or copper foil have been found to be most suitable for release material at low pressures.

One example will be shown of tests made on aluminum foil of 0.001 in. thickness in an 8-liter bomb when acetone-air mixtures were used for tests. The rupturing pressures for openings of different sizes and concentration of acetone in air are given in Fig. 6. The rupturing pressure increases as the area of the opening is reduced. In this example, where the pressure must not exceed 10 lb, the curves show that the diaphragms must be at least 3 in. in diameter if this aluminum foil is used, and the number of release openings should be such as to give 5 sq in. of diaphragm opening per cubic foot of space in the equipment.

The pressure required to rupture a given diaphragm material is directly proportional to the ratio of the perimeter to the area. This relation can be expressed by the equation

$$P = K(S/A),$$

in which P is the pressure required in psi to rupture the diaphragm, A the area in in.², S the perimeter in in. and K a constant characteristic of the particular diaphragm material being used.

In practice, K is determined for any given diaphragm material by making tests of the material in an opening of any given size and determining the pressure developed when the

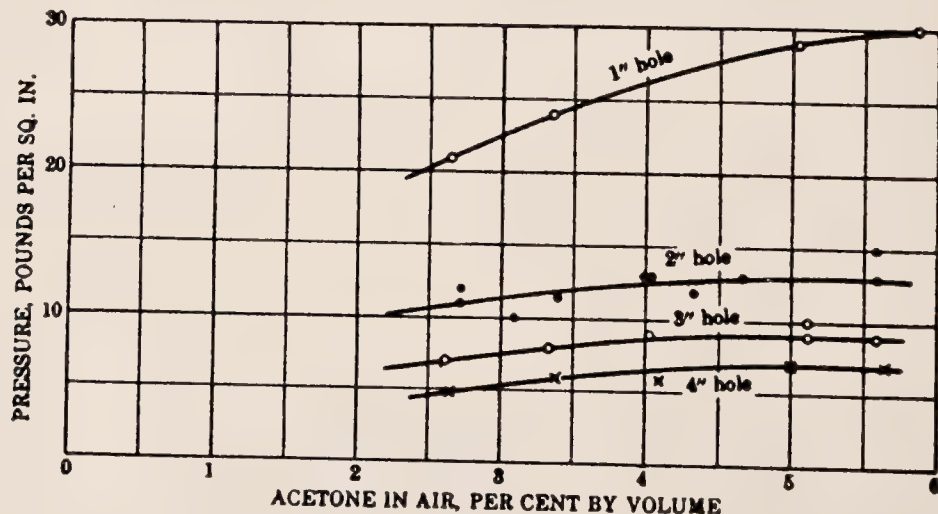


FIG. 6. Tests of aluminum diaphragms, 0.001 in. thick

diaphragm is ruptured. The determined value of K can then be used to calculate the rupturing pressure for openings of any size.

In addition to the above requirements demanded of release diaphragms to maintain the maximum developed pressure below a given safe pressure, the location and distribution of the release diaphragms are very important. Experiments made in round ducts 12 in. in diameter and 15 ft in length with acetone and air mixtures showed that release diaphragms should be distributed so that they were not more than 10 ft. apart, and that every dead end and sharp bend needed a diaphragm release to prevent the building up of pressure at these points.

9. *Recorders for Determining the Concentration of Combustibles in Hazardous Atmospheres.* Combustible gas indicators or recorders should be installed in all equipment where hazardous concentrations of combustibles may be present, and sampling locations should be chosen so that samples may be taken from different locations. Equipment has been developed whereby samples may be taken periodically from twenty or more locations and recorded on one instrument.

It is not the purpose of this report to discuss the merits of indicators and recorders. There are recorders now marketed which operate on the thermal conductivity principle, others on the change in volume resulting from the burning of the combustibles in the sample, while others depend upon the increase of resistance of a glowing filament when operating in an atmosphere containing combustibles; the greater the amount of combustibles present the greater the temperature of the wire and therefore the greater the resistance.

The performance and success of any of these devices can be determined only by actual installation in a representative plant and calibration of the device by chemical analysis against the particular combustibles used in the process.

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A THERMODYNAMIC ANALYSIS OF THE RATE OF RISE OF PRESSURE IN THE OTTO CYCLE

GEORGE GRANGER BROWN

Department of Chemical and Metallurgical Engineering, University of Michigan, Ann Arbor, Michigan

Approximately two-thirds of the mechanical horsepower of the nation is developed by internal-combustion motors operating on the Otto cycle. In the ideal cycle (Fig. 2) the mixture is compressed adiabatically from 1 to 2, and the combustion is supposed to take place instantaneously at constant volume over the path 2-3. The burned gases then expand adiabatically from 3 to 4, at which point the exhaust valve opens and the mixture expands from 4 to 4', leaving within the cylinder that quantity represented by point 5. On the exhaust stroke from 5 to 6 most of the burned mixture is forced out of the engine cylinder, that volume represented by point 6 being retained in the clearance volume. The charge is then drawn in along the intake stroke from 6 to 1, and the cycle is repeated.

I. The Normal Cycle

The actual combustion does not take place instantaneously, but begins at a single point or zone where ignition occurs. Inflammation spreads rapidly throughout the entire mixture, with each succeeding part to be inflamed burning under conditions of higher pressure and temperature than the previous zone. Such a reaction is not a true homogeneous reaction in the sense that the gas is a single homogeneous phase during combustion, but only in the sense that the reaction takes place in a gas phase which is strictly a single phase only before and after combustion and is unaffected by surfaces. Such a reaction has been called "progressive homogeneous".² The combustion may be expressed diagrammatically, as in Fig. 1. Condition A represents that immediately before ignition. B represents the complete inflammation of Layer 1 and its expansion compressing the unburned gas ahead of the flame. Condition C represents the inflammation of Layer 2, which expands and compresses the burned gases in Layer 1 and the unburned gases ahead of the flame. The same procedure is indicated in a further stage of combustion in D.

If the combustion proceeds orderly in this manner at a moderately low rate, pressure is equalized throughout the gaseous mixture as the flame advances. The normal combustion Otto cycle is an idealized cycle, assuming this type of normal combustion to take place while the piston is at top dead center. Figure 3 indicates the specific properties of the first and last layers of the mixture to burn in this manner as computed

by the thermodynamic chart of Hershey, Eberhardt, and Hottel.¹³ The expansion and compression of the successive layers of gas burned in such a progressive combustion reaction establish a temperature gradient throughout the burned mixture, as may be computed¹³ and as has been measured.^{14,22}

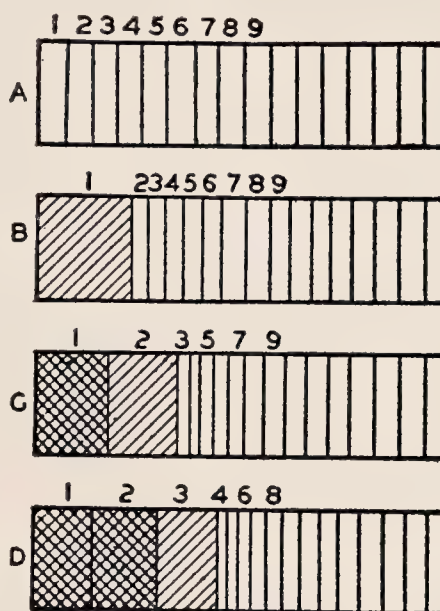


FIG. 1. Normal combustion. A represents the charge before ignition, B the conditions when Layer 1 is inflamed, C the conditions when the flame has passed 1 and 2 is inflamed, and D the conditions with a fast burning mixture when pressure is not uniform but is concentrated in the flame front.

The use of the enthalpy-entropy charts takes into consideration changes in heat capacity and equilibrium in the product of combustion. They are considered to give reliable results depending upon the assumption made in their application. For convenience the computations that may be made by the use of the ideal gas equation, ignoring chemical equilibrium, have been outlined in the appendices.

The temperature gradient at the end of normal combustion, assuming adiabatic processes and no mixing, with uniform pressure distribution during combustion with the piston at top dead center, is computed as 1500°F for ideal gas mixture see Appendix II(3)], and as 763°F by means of the thermodynamic equilibrium chart. In each case a compression pressure of 160 psi and a combustion pressure of 760 psi absolute

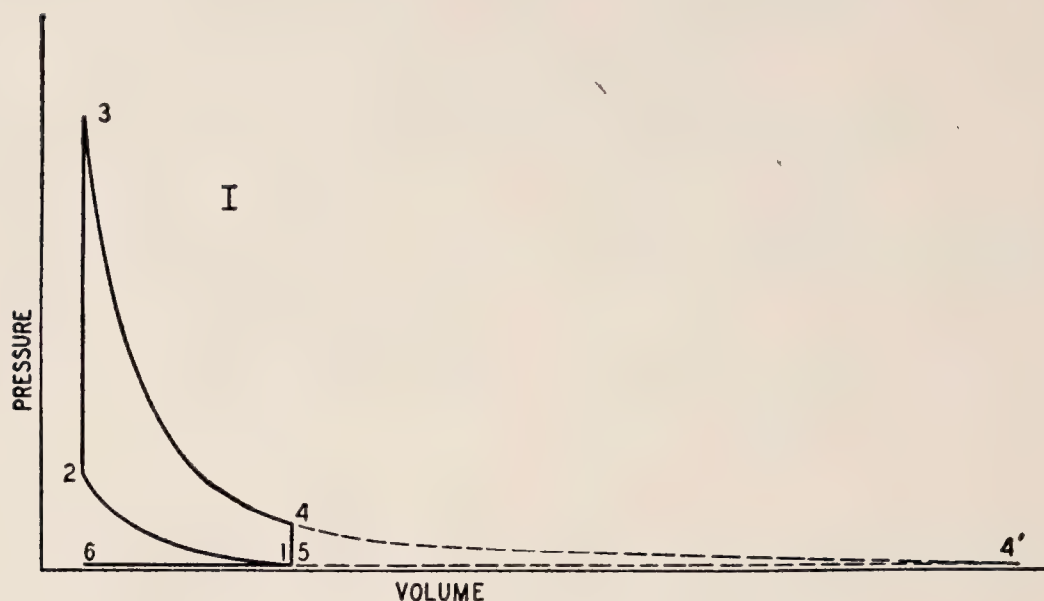


FIG. 2. Pressure-volume diagram of the ideal Otto Cycle I.

were assumed. The relatively large difference in the two methods is due to the fact that variations in heat capacity and dissociation have been accurately computed in the thermodynamic charts and neglected in the simple equations assuming ideal gases. An interesting comparison

with experimental data is provided from tests on an engine of 4.4 compression ratio, using 80 per cent of theoretical air²² in which a temperature gradient of about 600°F was measured. The computed temperature gradient for this compression ratio, using 85 per cent of the theoretical air according to the thermodynamic chart,¹³ is 1030°F. When it is considered that 40° of crank revolution was required for combustion in the engine, as well as that there were other differences, and that it is impossible to measure the temperature of the extreme first and last layers burned, the agreement appears satisfactory.

Insofar as efficiency and work are concerned, the ideal instantaneous combustion Otto cycle and the normal combustion Otto cycle are closely equivalent.^{13a} This is due to the fact that combustion occurs with the piston at top dead center in each case and with no important thermodynamic irreversibility other than that of the chemical reaction itself. These two cycles are identified as Cycle I of Fig. 2 and Cycle II of Fig. 3, as computed from the thermodynamic charts using 85 per cent of theoretical air.¹³ The properties of the working fluid at the various points as calculated are given in Table I. The slight differences between Cycles I and II indicated in Table I are due to the inexact but convenient use of arithmetical averages of the properties of the first and last layers of the mixture to burn. As the same procedure was used for the detonating Cycle III as for the normal Cycle II, these two cycles are comparable in all respects.

In these figures a solid line represents the average properties of the working fluid in the cycle. The dashed lines in Fig. 2 (Cycle I) indicate the specific properties of the fluid at the end of

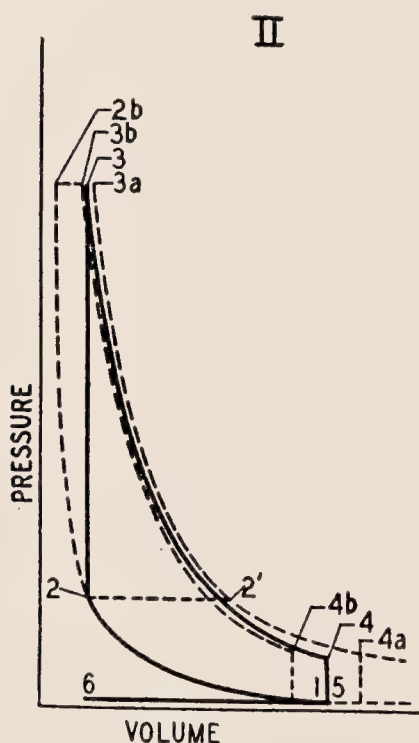


FIG. 3. Pressure-volume diagram of the normal Otto cycle. The solid lines represent average or effective properties, and the broken lines represent specific properties of the first (a) and last (b) parts of the mixture to be inflamed.

TABLE I
Computed properties of working fluid in adiabatic Otto cycle
Compression ratio = 6

Point	Cycle	Description	Absolute temperature, °R <i>T</i>	Absolute pressure, psi <i>P</i>	Volume of gases per lb. of air <i>V</i>	Relative enthalpy per lb. of air <i>H</i>	Relative internal energy per lb. of air <i>U</i>	Relative entropy per lb. of air <i>S</i>
1	I, II, III	Begin compression	650	14.7	16.8		26 _s	
2	I, II, III	End of compression						
2 _b	II	First to burn at constant <i>P</i>	1152	160	2.8	1836	138 _s	0.11 _s
2 _b	III	Last to burn at constant <i>P</i>	1640	760	About 0.9			0.11 _s
			1520	560	1.08	335 _s	228 _s	0.11 _s
3	I	End of combustion	4980	760	2.8		1585	0.576
2'	II, III	First to burn at constant <i>P</i>	4308	160	11.2	1676		0.633
2 _b '	III	Last to burn at constant <i>P</i>	4600	560	3.55	1792		0.564
2 _d '	III	Constant volume "detonating"	5255	2020	1.08		1675	0.520
		After equalization of <i>P</i>						
3 _a	II	First to burn	5475	760	3.08		1840	0.633
3 _b	II	Last layer to burn	4712	760	2.53	1836	1455	0.544
	II	Average 3 _a and 3 _b	5093		2.8		1647	
3 _a	III	First to burn	5430	725	3.25		1825	0.633
3 _b	III	Last to burn at constant <i>P</i>	4825	725	2.56		1520	0.564
3 _d	III	Constant volume "detonating"	4370	725	2.58		1350	0.52
	III	Average 3 _a , 3 _b , 3 _d	4875		2.8		1565	
4	I	End of expansion	3300	80	16.8		1010	0.576
4 _a	II	First to burn	3820	85	18.8		1180	0.633
4 _b	II	Last to burn	3060	85	14.8		940	0.544
	III	Average 4 _a and 4 _b	3440		16.8		1060	
4 _a	III	First layer normal	3800	80	19.8		1160	0.633
4 _b	III	Last layer normal	3200	80	16.2		980	0.564
4 _d	III	Detonating	2835	80	14.7		870	0.52
	III	Average 4 _a , 4 _b , 4 _d	3280		16.9		1003	
4'	I	End of exhaust		14.7	66	610	723	

expansion and with the exhaust valve open with the piston at lower dead center. The dashed lines in Fig. 2 (Cycle II) indicate the specific properties of the first and last infinitesimal layers to be inflamed, assuming adiabatic conditions without mixing and uniform pressure distribution during combustion.

II. The Knocking Cycle

If the inflammation is accompanied by an extremely high rate of rise of pressure so that the pressure is not uniformly distributed throughout the mixture, as has been indicated in Fig. 1 (D), which shows the Layers 4 and 5 immediately ahead of the inflamed Layer 3 compressed to a greater degree than the unburned gas toward the right end of the cylinder, a zone of high pressure is built up directly ahead of the flame and within the flame. Under these conditions the inflamed layers of gas at a high pressure expand very rapidly, compressing those layers of gas at low pressure in sequence with a velocity equal to the velocity of a sound wave in the gaseous medium.¹⁵ This action establishes a high intensity pressure wave traveling back and forth through the mixture and reflected from the walls of the combustion chamber. The immediate cause of such a pressure wave is the extremely high rate of rise of pressure developed in a part of the mixture and the extremely rapid expansion of this high pressure zone against the low pressure zone within the mixture. Such an expansion takes place with extreme speed and is thermodynamically highly irreversible, in that the work energy lost by the zone of high pressure equals

$$\int P_1 dV,$$

while the work done by the zone of high pressure on the zone of low pressure is equal to

$$\int P_2 dV.$$

Since dV is the same in the two expressions and P_1 is much greater than P_2 at the beginning of the expansion, although equivalent at the end, it is clear that the expansion of the high pressure zone against the low pressure zone is thermodynamically irreversible. However, the pressure immediately ahead of the high pressure zone is locally equal to P_1 , because of the high velocity of expansion and the high rate of rise of pressure. Therefore the path covered by the high pressure zone during expansion is correctly represented by an adiabatic path corresponding to the $\int P_1 dV$ above as is the $\int P_2 dV$ representative of the path for the low pressure zone.

The apparent loss in potential energy accompanying this irreversible expansion is evident in the high velocity intense pressure wave as kinetic energy, the conversion of potential energy into kinetic energy being necessary to accomplish the extremely rapid expansion caused by the high rate of rise of pressure in the high pressure zone.

In fuel-oxygen mixtures the rate of reaction and the rate of rise of pressure in the flame front are so intense that the condition outlined above is obtained in the case of an otherwise normal progressive combustion and results in the detonation wave,^{9,26} in which the unburned mixture immediately ahead of the flame front is ignited and inflamed by the intense adiabatic compression, so that the detonation wave is supported by the inflammation which is part of the pressure wave itself.

In fuel-air mixtures the rate of reaction is retarded by the presence of diluent, and the true detonation wave is not ordinarily developed. However, in high-compression engines the compression of the unburned charge ahead of the flame front by the process of normal combustion in which the pressure is uniformly distributed in the manner described frequently brings the unburned charge to such a condition of temperature and pressure that it spontaneously bursts into flame, accompanied by an intensely high rate of rise of pressure due to the extremely rapid inflammation. The effect of this extremely high rate of rise of pressure caused by the auto-ignition, or "detonation", of the unburned charge results in the same type of spontaneous, thermodynamically irreversible expansion of the high pressure zone against the low pressure zone of gases in the combustion chamber immediately following such autoignition. This results in the intense pressure wave which is similar in most respects to the detonation wave described above, except that it is not accompanied by the simultaneous inflammation of an unburned mixture.

This mechanism of engine detonation has been indicated for many years on the basis of experiments in bombs,^{32,7} and has been confirmed by photographic studies of detonating mixtures in the combustion chamber of an engine.^{25,23} In these studies²³ normal combustion at 900 rpm required 36° of crank rotation or about 0.0067 second for complete inflammation. Knocking or "detonating" combustion under the same speed and other conditions required a total of only 22° rotation or about 0.0041 sec for complete inflammation. The normal combustion of approximately one-half by weight of the mixture required the same time in each case—about 0.0036 sec. But the autoignition of the last half of the charge in the knocking combustion required only about

0.0005 sec for complete inflammation. The photographs²³ clearly indicate that autoignition and inflammation of the last half of the charge during 0.005 sec takes place without observable change in the position of the previously burned gases, that is, at substantially constant volume.

In Fig. 4 is shown Cycle III, which represents the normal combustion of two-thirds of the explosive mixture followed by autoignition or detonation of the last third of the mixture, computed by means of the thermodynamic charts,¹³

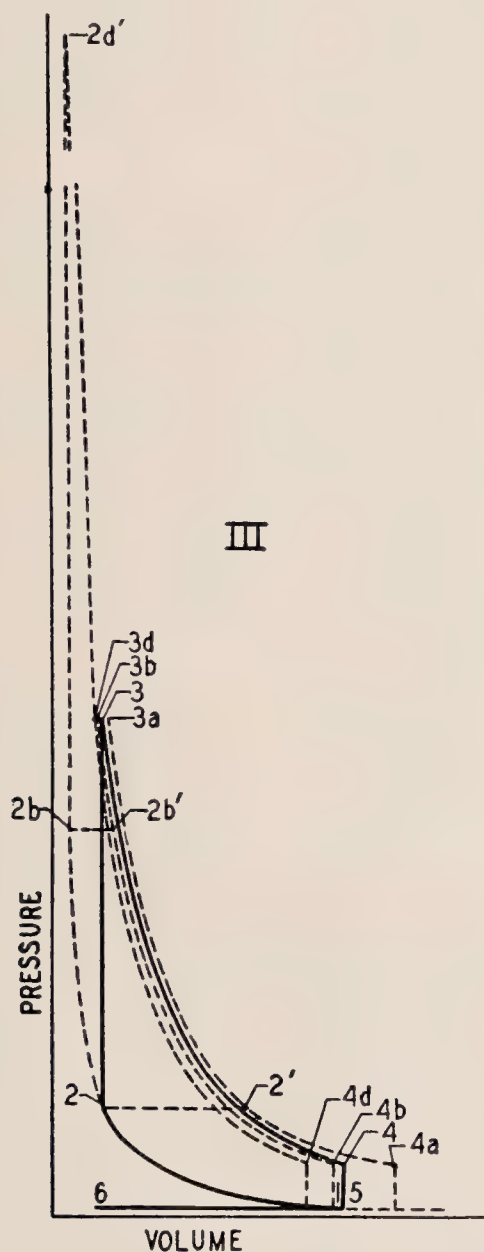


FIG. 4. Pressure-volume diagram of a knocking Otto cycle in which one-third of the charge detonates at constant volume. The solid lines represent average or effective properties and the broken lines specific properties of the first (a) and last (b) parts to burn normally with uniform pressure distribution and of the detonating (d) part of the mixture.

assuming 85 per cent of theoretical air and the same compression ratios and initial conditions as for Cycles I and II. The normal combustion of the first two-thirds of the mixture was assumed to take place with uniform pressure distribution throughout the charge, and the autoignition or knocking of the last third of the mixture to be inflamed was assumed to take place at constant volume. The entire process is assumed to be adiabatic, and the various zones of gases are assumed to expand or to be compressed without mixing under adiabatic conditions in the same manner as was assumed in computing the normal combustion of Cycle II¹³ represented in Fig. 3.

The properties of the working fluid corresponding to the different points in Cycle III are included in Table I. It will be noted that the compression of the charge along the path 1-2 is the same for all three cycles. The first infinitesimal layer to be inflamed is ignited under conditions corresponding to point 2 and burned with pressure constant and uniformly distributed throughout the mixture along the path 2-2'. Along this path the enthalpy of the mixture remains constant. Normal combustion proceeds in successive layers compressing the unburned mixture ahead of the flame adiabatically along the path 2-2b. At 2b the last layer is inflamed and burns at constant pressure 2b-3b. In Cycle II this completes the entire combustion. But in the knocking Cycle III this normal combustion is assumed to continue for only two-thirds of the charge, and upon combustion of the last layer to burn normally along the path 2b-2b', one-third of the charge, at conditions corresponding to 2b, is still uninflamed.

In Cycle III the balance of the combustion is assumed to take place at constant volume along the path 2b to 2d'. At the instant of the completion of this constant volume combustion or autoignition of the last third of the charge, that part of the charge which has burned normally is at the pressure represented by the horizontal line 2b-2b', while that part which has detonated is at the pressure 2d'. This large difference in pressure requires that the high pressure zone at the pressure 2d' expand with a high velocity along the adiabatic path 2d'-3d, thereby compressing the previously burned charge for the pressure 2b' to the point 3b for the last layer to be burned normally and to the point 3a for the first layer to be burned. After this expansion the mean effective pressure corresponds to point 3. This is the pressure which is effective on the piston in doing useful work, as the instantaneous high and low pressures in the high velocity pressure wave are not effective in accomplishing any useful work on the piston.

The computation for this adiabatic irreversible

expansion has been made in exactly the same way as was proposed by the authors of the charts¹³ for handling the irreversible expansion of the exhaust gases from the combustion chamber through the exhaust valve to atmospheric pressure at the end of the expansion zone. The temperatures and pressures of the various parts of the mixture so computed and listed as Table I indicate that the maximum temperature in the detonating combustion is found not in that part of the mixture to detonate (point 2d, Cycle III) but in the first layer of mixture to be inflamed (point 3a, Cycle III). This difference in temperature persists throughout the expansion stroke in the same manner as the temperature gradient in normal combustion Cycle II previously discussed.

The pressure developed in the detonating part of the charge is much higher than that effective in any other part of the mixture. In Table I an absolute pressure of 2020 psi is indicated for the detonating part of the charge, as compared with an effective pressure of 725 psi absolute for other parts of the charge. It is true that this high pressure in the detonating charge exists only for an extremely short interval of time and that it is not effective in doing work on the piston, although it has been referred to as an effective pressure because it is the motivating force for the high pressure wave which is set up in detonating explosions²⁵ and is accompanied by enormous acceleration in the pressure-time curve of the detonating portion of the charge.

If the observed time of autoignition at 900 rpm for one-half of the charge²³ be assumed as the time interval for the detonation of one-third of the charge in Cycle III, the average rate of rise of pressure during the detonation would be

$$\frac{2020 - 560}{0.0005} \text{ or } 2,920,000 \text{ psi/sec.}$$

The average rate of rise of pressure for the normal combustion preceding knock may be estimated as

$$\frac{560 - 160}{0.0036} \text{ or } 120,000 \text{ psi/sec.}$$

These figures indicate an average acceleration of the rate of rise of pressure during detonation or knock of about

$$\frac{2,920,000 - 120,000}{0.0005} \text{ or } 5,600,000,000 \text{ psi/sec/sec.}$$

Maximum acceleration of the pressure-time curve during detonation at speeds of 2000 rpm might be 10 to 500 times this estimated average.

Such forces exerted on the head and piston of the engine cause an accelerated deflection of engine parts, resulting in a maximum deflection greater than would be caused by the application of the same maximum pressure if the maximum pressure had been attained more gradually.¹⁶

These enormous forces developed by the detonating part of the charge have an intense local action on the surrounding part of the combustion chamber and may be the true cause for the destruction of part of alloyed pistons when operated under severe detonating conditions. The apparent fusion of such pistons in the detonating zone cannot be due to the temperature developed therein, as this is actually less than that developed in the first layer to burn (compare point 2d and point 3a of Cycle III in Table I).

The computed average effective pressure at the end of combustion for Cycle III is 725 psi, as compared with 760 psi for the normal Cycle II. This loss in effective pressure chargeable to the thermodynamic irreversibilities involved in the mass equalization of pressure following combustion results in a loss of about 5.5 per cent in net work, efficiency, and mean effective pressure of the cycle, as indicated in Table II.

The application of the ideal gas laws to the computation of such a knocking cycle¹¹ is indicated in Appendix II(4), with an indicated average pressure for the end of combustion (point 3) of 730 psi as compared with 725 psi for Cycle III computed from the charts.¹³

Since the power developed by such cycles depends entirely upon the increase in pressure accompanying combustion, it is interesting to note that the loss in work and efficiency due to knocking is proportional to the loss in effective rise in pressure upon combustion. This loss in

TABLE II
Computed effect of knocking on power and efficiency in adiabatic Otto cycle
Compression ratio = 6

	Normal	Knocking
Cycle	II	III
Work done = (U ₃ - U ₄) - (U ₂ - U ₁) averages, in Btu	475	450
Calculated efficiency based on 19,240 × 0.0749 Btu for net heat combustion of fuel per pound of air, in per cent	32.9	31.0
Mean effective pressure, in psi	182	172

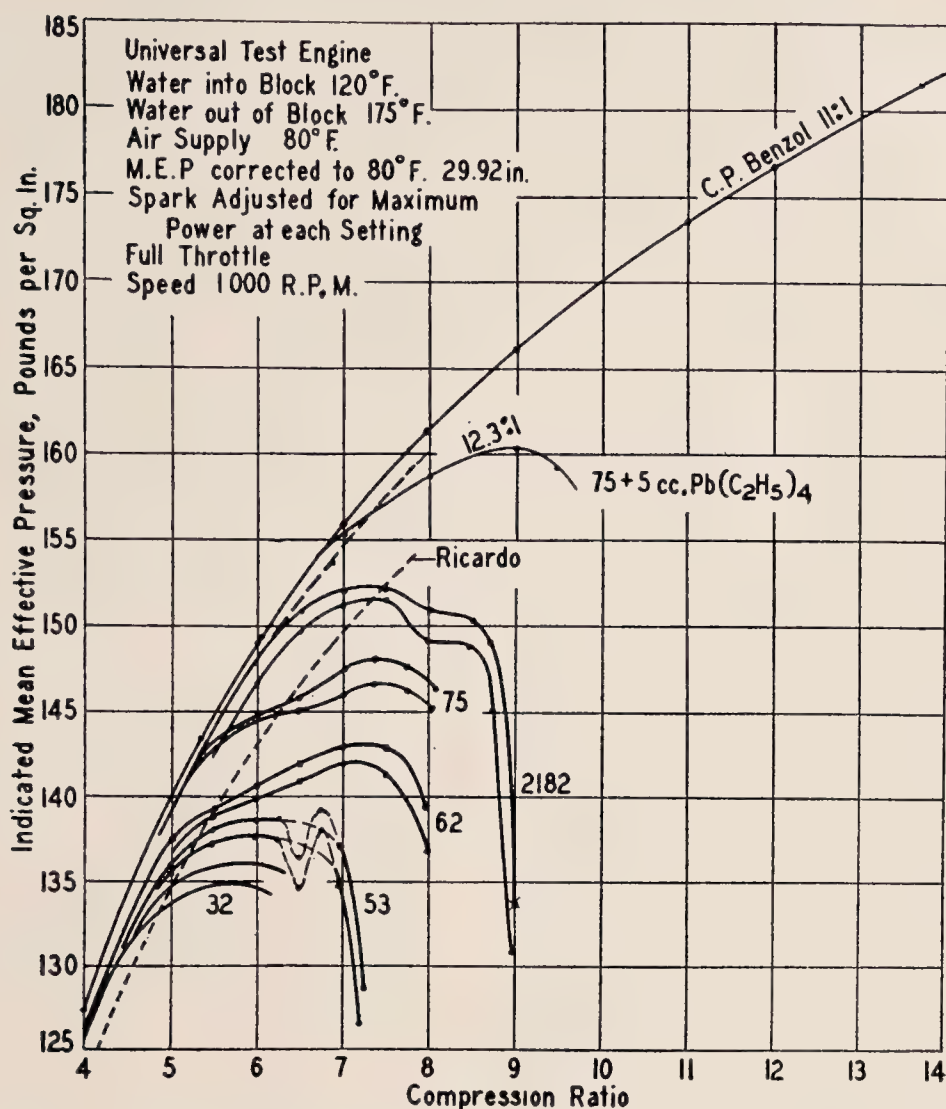


FIG. 5. The effect of compression ratio on the power (mean effective pressure) developed by different fuels in the NACA Universal test engine.

rise of pressure is computed as 5 per cent, using the ideal gas equation as in Appendix II, and 5.83 per cent as computed by the thermodynamic charts.¹³

An experimental confirmation of the loss in power due to detonation as computed upon these assumptions is provided by test data taken on a variable compression NACA Universal test engine and reported some years ago.³ Figure 5, reproduced herein, is a plot of the mean effective pressure as a function of compression ratio as observed for different fuels. Fuel 2182 developed incipient detonation at a compression ratio of about 6.

The increase in compression ratio beyond that at which incipient detonation develops, sufficient to cause detonation of one-third of the mixture as assumed for Cycle III, may be computed by Eq. (17) as derived in Appendix I(4), as has been done in Appendix II(4). As indicated therein,

an increase in compression ratio of about 33 per cent based on a compression ratio of 6.25 for incipient detonation, would be sufficient to cause the last third of the charge to detonate.

At a compression ratio of 8, which is an increase of 33 per cent over a compression ratio of 6, Fuel 2182 developed a mean effective pressure of about 151 psi, compared with a mean effective pressure of about 161 psi for benzene, which does not detonate under these conditions. The mean effective pressure developed by benzene is about 1 per cent greater than that developed by Fuel 2182 at lower compression ratios where neither fuel knocked. Making this adjustment for the different fuels, as indicated by the dashed extension of the curve for Fuel 2182 in Fig. 5, the loss in mean effective pressure caused by detonation of Fuel 2182 at a compression ratio of 8 is about 9 lb, as compared with a mean effective pressure of 160 lb for nondetonating

conditions. This corresponds to a loss of 5.6 per cent for the computed detonation of one-third of the charge. This is in excellent agreement with the 5.5 per cent computed for an idealized cycle by the thermodynamic charts¹³ as given in Table II.

Similar calculations for Fuel 62, which showed incipient detonation at a compression ratio of 4.7, indicates a loss in mean effective pressure of 5.3 per cent due to detonation at a compression ratio of 6.3, which is an increase of 33 per cent over that compression ratio required for incipient knock. Similarly, Fuel 75, showing incipient detonation at a compression ratio of about 5.3, indicates a loss in mean effective pressure of 5.1 per cent, due to detonation at a compression ratio of 7.1.

These results on different fuels of different knock ratings, showing approximately the same relative loss in mean effective pressure on detonation as computations based on adiabatic cycles, indicate that the loss in power and efficiency due to detonation may have a thermodynamic explanation in the loss of availability in the thermodynamic irreversibility of pressure equalization after detonation independent of any increased loss of heat by heat transfer from the gases to the jacket. The conversion of heat into work is a "second law" problem and is greatly reduced by thermodynamic irreversibility.

If the kinetic energy evident in the intense pressure wave caused by detonation were immediately converted to heat energy by absorption within the gaseous mixture, it might be expected that there would be no loss in power to the detonation. But the photographs of de-

tonating combustion in engines show that these pressures waves persist for some time,²⁵ and it would appear more reasonable to assume that they are damped by the absorption of their energy in the walls of the combustion chamber rather than by the mixture itself. The computation based on an adiabatic cycle confirms this interpretation. As correctly stated by Rassweiler and Withrow,²⁴ this loss in power and efficiency "must be accounted for by differences between knocking and nonknocking explosions other than a temperature difference of the gases", as they had observed that the temperature of the gases was actually lower in knocking combustion than in normal combustion. This difference is also evident in the computed Cycles III and II as indicated in Table I. Increased heat transfer due to the pressure waves following detonation may be an unnecessary assumption.

These pressure waves of high intensity developed by detonation must not be confused with the vibrations which are frequently observed in normal burning mixtures^{9,15} even if such vibrations take on the properties of a pressure wave,²⁶ owing to the acceleration of the flame⁹ and the accompanying intensification of the vibrations as it passes through the flame front. These vibrations are apparently caused by oscillations in the igniting spark²⁶; when suppressed or eliminated by proper control of the spark no shock wave was developed upon autoignition in a cylindrical bomb.²⁶

These pressure waves, combined with a high rate of rise of pressure in the last part of the mixture to burn, may be the cause of roughness in engines, as in bomb experiments this combina-

TABLE III
Quantitative comparison of smooth and rough engine (Ref. 17)

	Smooth	Rough	Relative
Maximum rate of rise:			
Pressure, psi/sec	162,300	34,000	2.18
Restoring force, psi/sec	188,370	465,000	2.47
Maximum acceleration in rise:			
Pressure, psi/sec/sec	93,000,000	567,000,000	6.1
Restoring force, psi/sec/sec	149,000,000	605,000,000	4.05
Relative kinetic energy of deflecting mass, (2.47) ²			6.10
Maximum restoring force, psi	439	543.7	
Maximum pressure, psi	410	410	
Shock factor,* per cent	7.07	32.6	4.6

* $\left(\frac{\text{Maximum restoring force} - \text{maximum pressure}}{\text{Maximum pressure}} - 1 \right)$.

tion was found to develop sound and vibrations in a similar manner.²⁶

III. Roughness

Intermediate in outward characteristics to knocking and normal combustion is another phenomenon characterized as "roughness", which is caused by high rates of rise of pressure or, more correctly, by high accelerations in the rate of rise of pressure. Janeway^{16,17} has analyzed combustion as related to roughness and has set forth the quantitative characteristics of two normal explosions (Table III), each developing the same maximum pressure with uniform pressure distribution throughout the combustion period, but one of smooth combustion characteristics and the other rough.

If the combustion chamber and location of the spark plug are so designed that the increase in volume of the flame with length of travel from the source of ignition is large during the early part of combustion and reduced during the later stages of combustion, the rate of rise of pressure is more nearly uniform with greatly reduced maximum acceleration.^{16,17} This makes for a smooth combustion and a retarded rate of rise of pressure during the combustion of the last part of the charge. This design is equivalent to igniting the mixture in a conical chamber by placing the spark plug centrally a short distance in from the base. The larger volume of the charge is then inflamed before it has been highly compressed by the expansion of previously inflamed mixture, and a much smaller part is burned under conditions which tend toward a high rate of rise of pressure. This tends to increase the acceleration in the rate of rise of pressure during the early part of combustion and to reduce the high acceleration which would otherwise occur in the last part of the mixture to be inflamed. The result is a smooth combustion which is otherwise difficult to obtain in high-compression motors.

Roughness may result from a high acceleration of the rate of rise of pressure from any cause, and should not be considered simply a mild form of detonation, which apparently always involves autoignition. The cause of roughness may be a distortion of the engine parts,^{16,17} similar to but much less severe than that accompanying detonation, which sets up a vibration, or it may be caused by a transverse vibration of the crankcase which passes through a cycle in the same time as the periodic force which produces it, thereby increasing in amplitude from cycle to cycle until the damping forces become equal to the exciting force.¹²

IV. The Rate of Rise of Pressure

In order to control roughness, it has been found necessary to limit the maximum acceleration in the time rate of rise of pressure of the combustion. The rate of rise of pressure in the combustion is also a major factor in the control of detonation.

Combustion in the engine^{23,24} is, in all respects so far investigated, similar to the combustion of gaseous mixtures in bombs of constant volume.^{15,26} The high degree of turbulence present in high speed engines and absent in bombs serves to increase greatly the speed of inflammation in normal combustion without appreciable change in the mechanism of combustion. This indicates that the reaction is heterogeneous in nature, that is, involving gases in more than one phase at one instant, and that the mechanism of the spread of flame through the mixture involves the transfer of heat or of material substance from unignited gases ahead of the flame.

The results of computations based on the ideal gas laws are qualitatively correct in analyzing the Otto cycle and may also be used to indicate the effect of some factors controlling the rate of rise of pressure during combustion. By this procedure,⁴ which is briefly summarized in Appendix I(5), it may be shown [Eq. (20)] that the rate of rise of pressure varies directly as some power of the pressure at which the gas is ignited.

The effect of temperature is more complicated but it has been shown^{4,21} that there is a real positive critical initial temperature at which the explosion develops its maximum rate of rise of pressure. This is true whether this critical initial temperature is determined under conditions of constant initial pressure, as is the case when the temperature of the mixture in the intake manifold is varied at constant throttle and speed, or under conditions of constant density, as is the case when the mixture temperature is varied after a positive supercharger or after being confined within the cylinder. But the critical temperature is not the same under these different conditions.²¹

V. Fuel Characteristics

Autoignition develops a very high rate of rise of pressure with loss of available work energy and is by its nature a different reaction from normal combustion. It has been indicated⁷ that the tendency of a fuel to knock in an engine may be estimated as varying directly with its rate of rise of pressure upon normal combustion and inversely with its ignition temperature. The rate of rise of pressure is directly proportional to the rate of reaction, which is also related to the "ignition lag",²⁸ so that perhaps all of us are really talking about the same thing but using different language.

In any case, it appears that both factors must be considered in autoignition, although only the rate of reaction need be considered in the case of normal combustion and the detonation wave.

In actual engine operation it is frequently observed that cracked petroleum fuels of an unsaturated and aromatic character are apparently depreciated in antiknock quality as compared with that which would be expected from laboratory tests. It has also been observed that supercharged engines do not so depreciate these fuels. It has been shown²¹ that a supercharged engine is operating above the critical initial temperature for maximum rate of rise of pressure, while the normal engine is usually operating below. If the knocking tendency of a fuel is a function of autoignition temperature and rate of rise of pressure (or reaction), the knocking tendency would be increased more noticeably by an increase in temperature in the normal engine, which is below the critical initial temperature, than by an increase in temperature in the supercharged engine, which would tend to decrease the rate of rise of pressure and thereby tend to compensate for the other effects of temperature in stimulating autoignition. These observations would be particularly applicable to aromatic fuels, because of their high autoignition temperature.¹⁹

In at least one case¹⁰ it was found that engine detonation could be eliminated by increasing the inlet temperature when operating at high temperatures, which would be expected if the operation were conducted at a temperature above the critical initial temperature and with a fuel of high autoignition temperature.

VI. Summary

The thermodynamic approach to combustion and the rate of rise of pressure in the Otto cycle are fruitful in analyzing the effect of different conditions upon the operation of the cycle. It is suggested that the thermodynamic method is an important tool in explaining and analyzing known characteristics such as "engine knock", roughness, and the effect of supercharging on the relative knock ratings of different types of fuels, and also a means of predicting characteristics of such combustion cycles as in the case of the critical initial temperature giving maximum rate of rise of pressure.

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APPENDIX I

1. The Increase in Pressure on Combustion

Assume an ideal gas with constant specific heats to which heat is added equivalent to combustion.

V_A = the constant volume of the combustion chamber,

V_1 = the volume of a portion of the mixture before combustion,

V_2 = the volume of this portion after combustion,

Q = the heat liberated by combustion of unit volume of mixture,

QV_1 = the quantity of heat available to V_1 liberated by combustion of V_1 ,

$$QV_1 = \Delta U_1 + W \quad (1)$$

ΔU_1 = the increase in energy content of the portion of mixture burned, evident in increased temperature,

W = the work done by V_1 on $V_A - V_1$ due to expansion of V_1 to V_2 ,

$$\Delta U_1 = \frac{P_2 V_2 - P_1 V_1}{K - 1} = (T_2 - T_1) C_v \quad (2)$$

$$W = \frac{P_2(V_A - V_2) - P_1(V_A - V_1)}{K - 1} \quad (3)$$

$K = C_p/C_v$ = ratio of specific heat at constant pressure to that at constant volume,

$$\begin{aligned} QV_1 &= \frac{(P_2 - P_1)V_A}{K - 1} = \frac{V_A \Delta P}{K - 1} \\ &= \frac{V_A \Delta P C_v}{R} = \frac{T_A \Delta P C_v}{P_A}, \quad (4) \end{aligned}$$

$$\Delta P = \frac{QV_1 P_A}{C_v T_A} = \frac{QV_1 R}{C_v V_A} = \frac{QV_1 R r}{C_v V_0}, \quad (4a)$$

where r = the compression ratio V_A/V_0 and V_0 = the volume of the charge prior to compression.

The increase in pressure (ΔP) is directly proportional to the portion burned (V_1) and the initial pressure (P_A) and inversely proportional to the heat capacity (C_v) and the original or initial temperature (T_A). For constant intake conditions (V_0), the increase in pressure (ΔP) upon combustion varies directly as the fraction burned and the compression ratio (r) and inversely as the heat capacity (C_v).

2. The Specific Volume of a Small Unit Mass of the Charge (as Represented by an Individual Layer in Fig. 1) in Normal Combustion

Considering the combustion of successive infinitesimal layers with uniform pressure distribution as in normal combustion,

V_0 = the original volume of small unit mass of the charge,

V_c = the volume of such mass after being compressed adiabatically by the burning of other portions, and at which it is inflamed,

V_e = the volume to which such mass expands at constant pressure during inflammation and combustion, and

V_f = the final volume of such mass after further adiabatic compression by the burning of succeeding portions, the whole at P_f .

In the first step of adiabatic compression of unburned gas by previous combustion of other parts

$$V_c = (P_0/P_c)^{1/\kappa} V_0. \quad (5)$$

In the second step of combustion at constant pressure

$$QV_0 = C_p(T_2 - T_1) = \frac{P_c(V_e - V_c)K}{K - 1}, \quad (6a)$$

from which

$$V_e = \frac{Q(K - 1)V_0}{KP_c} + V_c. \quad (6)$$

In the third step of adiabatic compression of the burned gas by later combustion of other parts

$$V_f = (P_c/P_f)^{1/\kappa} V_e. \quad (7)$$

Substituting Eq. (5) into Eq. (6) and the result into Eq. (7) and rearranging

$$V_f = \frac{(P_c)^{(1/\kappa)-1} Q(K - 1)V_0}{(P_f)^{1/\kappa} K} + \left(\frac{P_0}{P_f}\right)^{1/K} (V_0). \quad (8)$$

3. The Pressure Developed in the Mixture Accompanying Detonation

If combustion of any part takes place with extreme speed so that pressure is not distributed, that portion so burning or "detonating" may be assumed to burn under conditions of constant volume. P_d = the pressure developed by "detonation" of that part of the charge burning at constant volume.

From Eq. (4), remembering that V_c now equals

total volume to burn at constant volume and that all of this volume does so burn ($V_1 = V_A$)

$$QV_0 = \frac{(P_d - P_c)V_c}{K - 1} \quad \text{and} \quad Q = \frac{P_f - P_0}{K - 1} \frac{V_0}{V_0}$$

$$P_d = \left(\frac{Q(K - 1)V_0}{V_c} \right) + P_c$$

$$= \left(\frac{(P_f - P_0)V_0}{V_c} \right) + P_c \quad (9)$$

$$T_d = \left(\frac{P_d}{P_c} \right) T_c = \frac{(P_f - P_0)V_0 T_c}{P_c V_c} + T_c \quad (10)$$

Consider that part of the charge burns normally with pressure uniformly distributed, followed by constant volume combustion without uniform pressure distribution, that is, "detonation" of the last part, and that the pressure is equalized after combustion, rather than during combustion, by adiabatic compression and expansion.

P_x = final pressure after equalization after "detonation,"

V_x = final volume of unit mass after such combustion,

V_{xn} = final volume of unit mass that burns normally,

V_{xd} = final volume of unit mass that "detonates," and

P_f = final pressure resulting from normal combustion as before.

Since the total volume of the entire charge

remains constant

$$\sum V_{xn} + \sum V_{xd} = \sum V_0.$$

Since the quantity burned in normal combustion is proportional to the increase in pressure [Eq. (4)],

$$\sum_{P_0}^{P_c} V_{xn} + V_{xd}(P_f - P_c) = V_0(P_f - P_0). \quad (11)$$

From Eq. (8)

$$\sum_{P_0}^{P_c} V_{xn}$$

$$= \int_{P_0}^{P_c} \left[P^{(1-K)/K} \frac{(P_f - P_0)V_0}{K(P_x)^{1/K}} + \left(\frac{P_0}{P_x} \right)^{1/K} V_0 \right] dP$$

$$= \frac{(P_f - P_0)V_0(P_c^{1/K} - P_0^{1/K})}{P_x^{1/K}}$$

$$+ \left(\frac{P_0}{P_x} \right)^{1/K} V_0(P_c - P_0), \quad (12)$$

$$V_{xd} = (P_d/P_x)^{1/K} V_c, \quad V_c = (P_0/P_c)^{1/K} V_0,$$

and Eq. (9) gives

$$V_{xd} = \left[\frac{(P_f - P_0)(P_c/P_0)^{1/K} + P_c}{P_x} \right]^{1/K}$$

$$\times (P_0/P_c)^{1/K} V_0$$

$$= [(P_f - P_0)(P_0/P_c)^{1-(1/K)} + P_0]^{1/K}$$

$$\times (1/P_x)^{1/K} V_0. \quad (13)$$

Substituting Eqs. (12) and (13) into Eq. (11), cancelling V_0 , and solving for

$$P_x^{1/K} = P_c^{1/K} - \frac{\{P_0^{1/K} - [(P_f - P_0)(P_0/P_c)^{1-(1/K)} + P_0]^{1/K}\}(P_f - P_c)}{P_f - P_0}, \quad (14)$$

$$P_x^{1/K} = \left[\left(\frac{P_c}{P_0} \right)^{1/K} - \frac{1 - \{[(P_f/P_0) - 1](P_0/P_c)^{(K-1)/K} + 1\}^{1/K} \left(\frac{P_f P_c}{P_0 P_0} \right)}{(P_f/P_0) - 1} \right] P_0^{1/K}. \quad (14a)$$

4. The Effect of Compression Ratio on the Quantity of Charge Detonating

If an engine is operated at such compression ratio as to be at the limit of normal combustion, that is, so that any higher compression would result in incipient detonation, the compression ratio at which any degree of knock will occur or the degree of knock for any other compression ratio may be estimated by the following equations: From Eq. (4a)

$$\Delta P = xRr/C_v V_0,$$

where x = the fractional part of charge burned and r = compression ratio V_0/V_A .

The pressure reached on completion of normal combustion of x part of the mixture

$$P_a + \Delta P = P_0(r)^\kappa + (xRr/C_v V_0). \quad (15)$$

For the same intake conditions with the same mixture to obtain the same pressure at end of normal combustion

$$P_0(r_1)^\kappa + (x_1 R r_1 / C_v V_0)$$

$$= P_0(r_2)^\kappa + (x_2 R r_2 / C_v V_0). \quad (16)$$

For the same pressure of combustion of the last layer to burn normally

$$P_b = P_0(r_2)^\kappa + (\Delta P/r_1)(x_2 r_2), \quad (17)$$

where P_b = absolute pressure of the last part to burn normally and P_0 = absolute intake pressure.

If chemical equilibrium be assumed for the products of combustion, similar calculations may be made by use of the thermodynamic charts,¹³ without assuming ideal gases. In computing the effects of detonation as indicated by these equations, the results are similar by both methods.

5. The Rate of Rise of Pressure on Combustion as Influenced by Conditions and Properties of the Mixture

Considering the ideal combustion at constant volume and writing Eq. (4) in the differential form, and dividing by " dt ", the time rate of rise of pressure (dP/dt),

$$\frac{dP}{dt} = \frac{P}{TC_v} \left(\frac{dQ}{dt} \right) = \frac{Phk}{TC_v}, \quad (18)$$

where C_v = heat capacity of products of combustion per unit of mixture,

t = time,

h = heat of combustion per unit of mixture, and

k = specific reaction velocity and number of units reacting per unit of mixture per unit of time.

It has been shown⁴ that, even in this ideal homogeneous reaction, k has a maximum value for any particular pressure at some finite positive temperature when the order of the reaction is greater than 1. This was demonstrated theoretically on the basis of the well-known effects of temperature and density upon the velocity of gaseous reaction, which lead to the following equation

$$k = C(P/T)^{a-1} e^{-B/T}, \quad (19)$$

where a = the order of the reaction,

B = a constant representing the "energy of activation," and

C = a constant of integration,

from which it may be shown that for any given pressure (P), k has a maximum value when $T = B/(a - 1)$.

Thus the well-known fact that the rate of flame travel,³² as well as the rate of rise of pressure,^{4,21} may be decreased by an increase in initial temperature may be explained on the basis of the well-known effect of temperature and density upon gaseous reactions.

Combining Eq. (19) with Eq. (18)

$$\frac{dP}{dt} = C \frac{h}{C_v} \left(\frac{P}{T} \right)^a e^{-B/T}. \quad (20)$$

By means of this equation it has been shown⁴ that there is a real positive value for the initial temperature (T) which will give the maximum rate of rise of pressure upon explosion of an explosive mixture for any given constant initial pressure P , and if the order of the reaction a is greater than 1, the same statement applies to mixtures which may be ignited under conditions of constant initial density.

Similar relationships leading to exactly the same conclusions can be derived by a more complicated procedure, assuming normal combustion or progressive inflammation by a self-propagating flame.

These conclusions have been verified by experimental work in bombs.^{4,21} Furthermore, the effect of heat capacity of the products of combustion and of their change with temperature upon the relative value of the initial temperature giving maximum rate of rise of pressure, has also been confirmed experimentally²¹ in bombs. The general conclusions regarding the "critical initial temperature" giving maximum rate of rise of pressure have also been confirmed by tests conducted in normal and supercharged engines.²¹

It is therefore indicated that the same thermodynamic or macroscopic approach may be used with satisfactory results in problems involving rates as well as those supposed to be at equilibrium.

APPENDIX II

Numerical Calculations Using These Equations Derived on the Assumption of Ideal Gases

If $K = 1.3$, $P_1 = 160$, $P_2 = 760$.

1. Compute Q (Btu per cubic foot at $P_1 T_1$): by Eq. (4), since $V_1 = V_A$

$$Q = \frac{P_2 - P_1}{K - 1} = \frac{(760 - 160)144}{(778)(0.3)} = 370 \text{ Btu.}$$

2. Calculate the ratio of the final volume of the last portion to burn to its initial volume: from Eq. (4)

$$Q(K - 1) = P_f - P_0$$

and $P_c = P_f$. Equation (8) becomes

$$V_{fL} = \frac{(P_f - P_0)V_0}{P_f K} + \left(\frac{P_0}{P_f} \right)^{1/K} V_0$$

$$\begin{aligned} \frac{V_f}{V_0} &= \frac{600}{760 \times 1.3} + \left(\frac{160}{760} \right)^{1/1.3} \\ &= 0.608 + 0.307 = 0.915. \end{aligned}$$

3. Calculate the ratio of the final volume of the first portion to burn to its initial volume. When

$$P_c = P_0$$

$$V_{fI} = \frac{(P_f - P_0)V_0 \left(\frac{P_0}{P_f}\right)^{1/K} + \left(\frac{P_0}{P_f}\right)^{1/K} V_0}{K(P_0)} \\ = \left(\frac{P_0}{P_f}\right)^{1/K} V_0 \left[\frac{(P_f - P_0)}{KP_0} + 1 \right]$$

$$\frac{V_f}{V_{0I}} = \left(\frac{160}{760}\right)^{1/1.3} \left[\frac{600}{160.13} + 1 \right] \\ = 0.307[3.88] = 1.19.$$

Since this is an ideal gas and the initial temperature T_0 was the same for all parts of the mixture and V_0 was likewise the same, it follows that

$$T_{fI} = T_0 \times (P_f/P_0) \times (V_f/V_0)_I.$$

$$\text{If } T_0 = 1150^\circ\text{R}, T_{fI} = 6500^\circ\text{R}, T_{fL} = 500^\circ\text{R}.$$

4. Assuming that the last third of the charge burned were to "detonate" and that the quantity of charge burned normally is directly proportional to the increase in pressure in normal combustion, the final pressure after equalization may be computed by equation 14 or 14a derived on the assumption that the working substance is an ideal gas.

$$P_x^{1/1.3} = \left[\left(\frac{560}{160}\right)^{1/1.3} - \frac{1 - \left[\left(\frac{760}{160} - 1\right)\left(\frac{160}{560}\right)^{0.3/1.3} + 1\right]^{1/1.3}}{\frac{760}{160} - 1} \left(\frac{760}{160} - \frac{560}{160}\right) \right] 160^{1/1.3} \\ = \left[2.621 - \frac{1 - (3.75 \times 0.75 + 1)^{1/1.3}}{3.75} (4.75 - 3.5) \right] 160^{1/1.3} \\ = \left[2.621 - \frac{1 - 2.797}{3.75} 1.25 = 3.22 \right] 160^{1/1.3} \\ = 159.5 \\ P_x = 730.$$

This represents a loss of 30 lb out of 600 lb pressure rise, or 5 per cent.

5. Compute the compression ratio (r_2) that would cause the last third of the charge to detonate if the compression ratio of r_1 is just insufficient to cause incipient detonation.

From Eq. (4)

$$Q(K - 1) = (P_b - P_1).$$

For adiabatic compression

$$P_1/P_0 = (V_0/V_1)^K = (r_1)^K.$$

For incipient knock

$$Q(K - 1) = P_b - P_0(r_1)^K.$$

From which r_1 may be determined by sub-

stituting the numerical values

$$\frac{370 \times 778}{144} (0.3) = 760 - 14.7 (r_1)^{1.3}$$

$$r_1 = 6.25.$$

Substituting the numerical values in Eq. (17)

$$760 = 14.7 (r_2)^{1.3} + \frac{600}{6.25} \left(\frac{2}{3}r_2\right)$$

$$r_2 = 8.3.$$

This corresponds to an increase in compression ratio of 33 per cent at 6.25 ratio to cause the last third of the charge to detonate as referred to the compression ratio just short of incipient detonation.

CHEMISTRY OF OTTO-CYCLE ENGINE COMBUSTION

HAROLD A. BEATTY

Ethyl Gasoline Corporation, Detroit, Michigan

Chemical study of internal-combustion engines is amply justified from the theoretical as well as the practical point of view. Aside from their obvious economic importance, engines have provided a wealth of information regarding the nature of combustion, much of it unattainable with other conventional forms of laboratory equipment. In return, the interpretation of these results has been—and to a large extent still is—a complex problem which challenges those chemists who are interested in the general theory of the subject.

Nevertheless, it seems fair to say that, until recently, there has been in general a lack of effective cooperation between the chemists on one hand and the engineers on the other, and advances in the theory of engine combustion have been slow. This seems to have been due largely to a tendency, on both sides, to oversimplify the problem. Chemists have made numerous laboratory experiments under conditions not remotely resembling those of an engine, but the results were applied, without criticism, directly to engine combustion; at the same time no detailed analysis has been made of the chemical facts furnished by the engine itself. On the other hand, engineers have been largely occupied with the practical development and testing of engines and fuels, with little or no direct investigation of the chemical theory of the subject.

Recent years have seen considerable improvement in these respects. Chemical experimentation conducted directly with engines or closely related apparatus has given a series of facts to replace uncertain assumptions; simultaneously, the development of the chain reaction theory of the slow oxidation and explosion of gases has provided a reasonable basis for the explanation of the phenomena observed. As a result, it is now possible to advance a general outline of the nature of engine combustion which is in accord with the known facts and appears to be theoretically sound. At the same time, a great many details remain to be filled in and a number of major points are still in doubt.

It is the purpose of this paper to present, briefly, such an outline, to indicate some of the respects in which our knowledge is still deficient, and to emphasize further the relative complexity of engine combustion. It is hoped that this survey will to some degree promote better appreciation of the problem and encourage still more effective cooperation between the chemists and engineers who are concerned with it. We shall consider in our survey only the Otto-cycle en-

gine, since the Diesel engine will be dealt with in other papers of this symposium. No attempt will be made to refer to the extensive literature on the subject, either in its entirety or specifically. (For recent selected bibliographies see the appropriate sections of *Science of Petroleum*, Oxford University Press (1937), *Proceedings of the Second World Petroleum Congress*, Paris, 1937, and this Symposium; also References 1, 2, and 3.) Only those data and conclusions which have been instrumental in establishing our present conception of the subject have been selected; their interpretation is the present author's personal one, but appears to be in general accord with the consensus of opinion.

Normal Combustion

Normal combustion in an engine comprises the spark ignition and subsequent slow inflammation of the charge, followed by equilibrium changes in the burned gas. Due to the method of operation, the hydrodynamic and thermodynamic aspects are highly complex, but the chemistry appears to be no more complicated than that of the similar inflammations which have been investigated by various laboratory methods.

First, the air-fuel mixture, containing the slight excess of fuel required for development of maximum power, is mixed with more or less exhaust gas, compressed to over 5 atm, and ignited by the spark. The mechanism of this ignition is a specific problem, and has been considered in foregoing papers in this symposium. In the engine there appears an ignition lag, which may be defined as the period, following the initial spark, during which no reaction is detected visibly or otherwise. The lag is about 1 millisecond or less, and does not seem to vary greatly with the fuel used. This subject has not been studied in any detail, and might well repay closer investigation. It is obvious that reactions of some kind are taking place during the lag, and information as to their nature might be obtained from correlation of lags with other combustion characteristics of the charge, such as normal flame speed and knocking tendency.

The flame front then travels through the charge, accelerating rapidly to a speed of the order of 100 ft per second, then slowing down near the end of its passage; it is highly irregular in shape, owing to turbulence. For the type of air-fuel mixtures used in engines, there is as yet no exact solution of the problem of flame speed;

we can only assume that the inflammation is a chain-reaction process in which the interaction between the chain carriers and the reactant molecules requires a considerable energy of activation, that is, the fuel molecules are relatively stable and slow to react. Thus, ahead of the flame front, the chains are broken until the resulting general temperature rise furnishes the surplus energy necessary for further chain extension. Then the flame velocity is a function of such variables as the number of chain carriers emitted, their available energy, and the surplus energy of activation required. These quantities, in turn, are dependent, in order of increasing importance, on the pressure, temperature, and composition of the unburned gas.

In an engine these variables are continuously changing in the gas ahead of the flame front, and the flame velocity might be expected to show a regular increase as combustion proceeds. But these effects are not noticed, since the true mass or transition velocity is much less than the actually observed space velocity, owing to the turbulence of the charge. Hence, in engines, the visible flame speed is determined almost wholly by engine speed and the corresponding turbulence. Changes in composition of the charge, including dilution by exhaust gas, have some effect, variations in charge temperature and pressure have little or no effect, and the presence of small amounts of antiknock compounds is not noticeable.

Combustion of the fuel is practically complete within the narrow flame front; behind the flame front, as the temperature falls, shifts occur in the equilibria between the reaction products. The corresponding pressures and temperatures at different points in the burned gas have been experimentally determined, and are in accord with this mode of combustion. The pressure rise is smooth and noiseless; its maximum rate is of the order of $1000 \text{ psi} \times \text{msec}$. The flame spectrum is normal, and shows the C—C and C—H bands.

Abnormal Combustion

As the "severity" of engine conditions—the pressure, temperature, and heating time of the charge—is increased, the fuel no longer remains entirely inactive, but instead tends to react spontaneously in one way or another, leading to an abnormal type of combustion. The type obtained depends both on the particular engine conditions and on the chemical nature of the fuel. We distinguish, roughly, three different types: preignition, afterfiring, and knock.

In preignition the charge, on coming in contact with some hot spot, such as the exhaust valve, ignites prior to passage of the spark, and if this

occurs early enough in the cycle, there is back-firing into the carburetor. Some fuels, notably benzene and methanol, tend to preignite under the same conditions under which other fuels tend to knock. This distinction is not only of practical importance but has obvious significance in the theory of combustion. As might be expected, the addition of antiknock compounds such as tetraethyllead has but a slight effect, often detrimental, on the preigniting fuels; the organic antiknock compounds have not been tested extensively. In this connection laboratory tests of ease of ignition by a hot wire or the like might prove valuable; the time of heating should be very short.

In afterfiring the spark may be cut out and the charge continue to ignite by compression. It is not clear to what extent this phenomenon is a form of preignition or is a form of knock. It can be regarded as a sort of delayed preignition, but there may be some effect on adding an anti-knock agent, depending on the type of fuel used; this might well be investigated in machines of the adiabatic-compression type where the operating variables, especially the temperature, can be better controlled.

Knock is a form of spontaneous ignition, starting at one or more points in the "end gas" or unburned charge ahead of the flame front. The amount of charge entering into knocking combustion may vary from an indistinguishably small portion to at least three-quarters of the whole; also, apparently, the intensity or rate of knock may vary considerably. The knock flame seems to sweep through the remaining unburned charge, with a velocity in the neighborhood of 1000 ft. per second—a value far greater than that of the normal flame, but much less than would be calculated for a true detonation wave in similar air-fuel mixtures. Correspondingly, the rate of pressure rise is high, the maximum value being of the order of $10,000 \text{ lb per ft}^2 \times \text{msec}$, and the change in the rate of pressure rise is sufficiently abrupt to set up pressure waves, which induce the emission of sound waves from the engine. The spectral emission of the knocking flame resembles that of the normal flame, but it has a greater extent and intensity and the characteristic hydrocarbon C—C and C—H bands are weak or disappear. The normal flame prior to knock is indistinguishable from that observed in the entire absence of knock.

In nonknocking operation no indication is found of any extensive chemical change in the end gas. As conditions are changed in the direction to produce knock, formaldehyde appears in the end gas in increasing amounts, which may vary for fuels of equal knock intensity. Compounds of the peroxide type are also present, but

the amount of oxygen consumed is small. Suppression of knock by addition of aniline eliminates the formaldehyde, but with tetraethyllead, it is stated, this effect is not obtained in the engine. Both antiknock agents suppress the formation of those unidentified compounds which, under conditions of incipient knock, give a continuous absorption in the spectrum of the end gas.

Factors in Knock

By and large, any changes which increase the temperature, pressure, or heating time of the charge, or modify its chemical composition in the direction of readier ignition, tend to promote abnormal combustion of one type or another. In the case of knock, any variations which would be expected to favor preflame oxidation of the end gas are found to promote knock. Because of its greater interest, subsequent remarks will be confined to the phenomenon of knock.

The relative importance of the time, temperature, and pressure factors is difficult to estimate, since they are not readily susceptible of independent variation in an engine and the functions relating these variables to the occurrence of spontaneous ignition remain entirely unknown for time periods as short as those in an engine. Recent work on spontaneous ignition indicates that the pressure as well as the temperature is an important factor, and it is to be hoped that further information will be obtained for shorter time lags. In the engine the pressure and heating time for the end gas can be quite accurately measured; the time is of the order of 1 to 10 msec. The temperature ahead of the flame has only been estimated approximately, but probably exceeds 500°C; it will doubtless be desirable, later, to determine this more accurately.

Equally important in determining the onset of knock is the chemical composition of the charge, including the nature of the fuel, the air-fuel ratio, dilution with exhaust gas, and the presence of proknock or antiknock compounds. The pronounced effect of the molecular structure of the fuel is well known, but the explanation of this effect is still far from complete. As to air-fuel ratio and charge dilution, it is difficult to determine to what extent these factors have a direct, chemical influence on the oxidation and ignition of the end gas, and to what extent they act indirectly by virtue of their effects on the velocity and temperature of the normal flame.

The influence of proknock and antiknock compounds is conspicuous: as little as one molecule of tetraethyllead in over 200,000 molecules of hydrocarbon may be sufficient to give a noticeable decrease in knock. Proknock compounds usually either contain active oxygen or else

react readily with air to yield it; some other compounds, such as certain bromides, are also effective. Antiknock agents are mostly metals or organometallic compounds, and a series of aniline derivatives. On a molecular basis the former are of the order of one hundred times as effective as the latter, the distinction being so marked as to suggest a fundamental difference in their modes of action. The relative and the absolute effectiveness of an antiknock agent may vary considerably, both for different fuels and for different operating conditions; for a given fuel the effectiveness is not directly proportional to the amount added, but tends to approach a limiting value.

In general, the characteristics of the knocking flame, particularly its spectrum, are the same, regardless of which factor (increase in time-temperature-pressure, or change in chemical composition of the fuel, or decrease in the amount of antiknock agent) is responsible for its occurrence, and we conclude that all these factors are concerned with the initiation rather than the propagation of the flame.

The physical and chemical factors are often interrelated; thus the effect of a specific change in engine conditions is by no means necessarily the same for two different fuels, or for a given fuel with and without an antiknock agent added.

In addition there may be other factors, such as the effect of radiation or ionization from the flame front, the turbulence of the end gas, or the nature of the engine walls in contact with the end gas. These do not appear to be important; however, little is known about them, and it is quite possible that turbulence, in particular, may be a significant factor. There is as yet no particular evidence for the existence in the engine of surface effects of the chain-reaction type. The fact that such effects may be controlling factors in many slow oxidation reactions which have been studied by laboratory methods is no *a priori* reason for their importance in an engine, where conditions are widely different. The strictly thermal effect of surface, particularly of hot spots, is of course conspicuous.

Theory

The foregoing facts readily suggest their own general explanation, and the hypothesis that knock results from a spontaneous ignition of the unburned charge was advanced at least thirty years ago. However, the lack of correlation between the knocking tendency and the spontaneous ignition temperatures of different fuels, alone or with antiknock compounds present, casts doubt on the correctness of the hypothesis. This doubt disappears when the meaning of the

term "spontaneous ignition" is analyzed, and it is realized that relative values measured under one set of conditions, as in some specific laboratory method, cannot be applied to widely different engine conditions; any attempt to extrapolate such values to reach engine conditions is insecure, owing to the chain-reaction nature of the processes involved.

The general theory is, then, about as follows: Before the arrival of the flame front, slow oxidation occurs in the end gas by a chain-reaction mechanism. In normal combustion the amount of such oxidation is slight, and the products formed have no important effect on the subsequent inflammation. Doubtless the rate of such oxidation is not constant and increases with time, but before the ignition point is reached the arrival of the flame completes the combustion. When the conditions are such that knock will occur, then the rate of oxidation is greater, probably owing to greater efficiency of chain extension, and it increases until the critical point is reached where the coefficient of chain branching becomes unity. There is then a sudden very considerable increase in the concentration of activated partial oxidation products in the end gas. It may be that this reaction itself is the actual ignition, and that the completion of the combustion and the appearance of flame take place in conjunction with it, throughout the charge. Or, as seems more likely, it may be that the partial oxidation reaction merely gives a mixture which is far more inflammable than the original mixture. Its combustion may then be abruptly completed, as another step, by a flame which starts from one or more favorable points and is able to spread at a rate far greater than normal; that is, the combustion may be regarded as a kind of two-stage process. Thermodynamically, these alternative modes of ignition—by local action or by a moving flame—are practically identical, and there is no essential chemical distinction between them; the important point is that in either case the ignition is a result of a sudden change in the chemical composition of the gas, and not of a final critical increment in temperature alone. If we grant the presence of a moving flame of knock, it seems reasonable to expect this to start from the normal flame front, where the available energy is greatest, and the photographs suggest that this does occur in many cases. But it need not do so, since the development of the preliminary branched-chain reaction is probably not uniform throughout the end gas, and as a result that part of the gas which first attains the condition of extra-inflammability and ignites, may be well removed from the normal flame front.

The occurrence of a moving flame having a

velocity intermediate between that of the normal flame and that of a detonation wave is not an unreasonable hypothesis. Although the inflammability of the mixture through which the flame of knock passes has become much greater than normal, there is no particular reason to suppose that it attains the degree of inflammability necessary for the propagation of a detonation wave. Such intermediate flame velocities are not usually observed in combustion experiments in tubes, etc., for the obvious reason that no chemical changes take place in the unburned charge in those cases; however, abnormal flame velocities or quasidetons have been observed when the ignition source provides a high surplus of energy.

Any attempt to make the foregoing description of knock more specific by defining the exact nature of the chain reactions involved and the products obtained possesses considerable uncertainty. Specific reactions have been proposed to describe the results obtained in slow oxidation and ignition of gases carried out under conventional laboratory conditions, but the actual chemical analysis of these reactions is far from complete. For the more drastic engine conditions practically no actual facts are available, other than the aforementioned presence of formaldehyde and other unidentified oxygenated compounds and the disappearance of the C—C and C—H bands in the subsequent inflammation. Correspondingly, any attempt to correlate the knock resistance of specific hydrocarbons with the mechanism of their slow oxidation is uncertain to the same degree, and there is as yet no sound reason for believing that the results obtained for these hydrocarbons under laboratory conditions can be applied to engine conditions without modification. The extent, if any, to which straightforward thermal decomposition of the fuel molecules influences the oxidation reactions preceding knock is unknown. It seems possible that differences in thermal stability may account for the variation in knocking tendency of some structurally similar hydrocarbons which would appear to be of approximately equal susceptibility to attack by oxygen. Investigations along this line are desirable.

The action of proknock and antiknock compounds is, of course, readily explainable on the basis of this theory of slow oxidation by chain reactions in the end gas. But here again, the specific mechanism of their action remains almost entirely unknown. The organic antiknock agents are presumably destroyed in the act of chain-breaking. If this can be confirmed, it is possible that valuable information as to the number and length of the chains can be obtained from a quantitative study of the effects of these agents.

There is a strong suggestion that the metallic atoms are able to break chains repeatedly, probably by virtue of alternate oxidation and reduction; it is reported that the absorption spectrum of the end gas shows atomic lead but no lead monoxide when knock is eliminated by the addition of tetraethyllead.

Complexity

The foregoing summary of the observed facts and general theory of engine combustion has failed to fulfil its purpose, if it has not sufficiently indicated the complexity of such combustion and given some indication of the chemical and mechanical problems which remain to be solved before a more detailed theory can be developed.

Actually, in engine studies, the principal variables under direct control are the speed, spark timing, and jacket temperature of the engine, and the pressure, temperature, and composition of the charge. As regards the end gas, any attempt to change one variable alone inevitably causes one or more of the others to change also, either directly, or indirectly by affecting the speed or temperature of the normal flame. Other factors, such as the turbulence and the nature of the combustion chamber surfaces, cannot be closely controlled during the progress of a run. The effect of such uncontrollable factors, or of slight variations in the controlled variables, leads to considerable irregularity in the combustion from one explosion to the next. This is clearly shown, photographically and otherwise, even by engines operated under rigidly specified conditions; the flame speeds and temperatures, for example, may vary by as much as 5 or 10 per cent. This complexity makes both the correlation and the analysis of results very difficult.

On the other hand, laboratory experiments conducted in special equipment and under carefully controlled conditions so far have failed to come anywhere near duplicating engine conditions, and, as previously pointed out, the relations between the different conditions are uncertain to a high degree. For example, ignition temperatures may be measured in the conventional manner, with a time lag of one second to one hour or more, during which time it is supposed that a certain necessary amount of slow oxidation takes place, and relations may be established between the pressure, temperature, etc., and the time lags. But this slow oxidation during the time lag may itself also have an induction period (probably largely conditioned by the combustion chamber surfaces) of the order of, say, 1 msec. Then the effect of the pressure, temperature, etc., on this short time

lag will be entirely overlooked in the laboratory experiment, but may be the paramount factor in the engine.

An analogous case occurs in Diesel combustion, where it can be shown that the flame starts in the vapor envelope surrounding the fuel spray, after a time lag whose origin is largely chemical and is not merely the time of evaporation and heating of the vapor. The dependence of this time lag on the pressure and temperature is by no means a linear or simple function.

An even worse situation arises when we have the possibility of simultaneous reactions, with different pressure or temperature coefficients, and this probably is the case in the slow oxidation of the higher hydrocarbons. A further complication is that under certain conditions such reactions have a negative temperature coefficient over a certain temperature range. To what extent this effect applies under engine conditions is uncertain, but there is evidence that under some conditions an increase in temperature may reduce the possibility of knock, while increasing that of afterfiring.

Examples. The result of this engine complexity is well illustrated by the ambiguity which arises in determination of the absolute or relative knock ratings of different fuels or pure hydrocarbons. An example of the magnitude of the variations which can be obtained for two pure structurally similar hydrocarbons is furnished by the following data from the recent results of Heron and Gillig of this Laboratory.¹ The data give the effects of engine speed and jacket temperature on the *ratio* of the maximum power output obtained from diisobutylene to that from isooctane (2,2,4-trimethylpentane), when run in a supercharged test engine, with the inlet pressure increased until the fuel fails by giving abnormal combustion. At 900 rpm this power ratio falls from 1.64 at a jacket temperature of 212°F to 1.01 at 350°F; at 1800 rpm the corresponding ratios are 0.90 and 0.82. Thus these moderate changes in engine conditions can effect a twofold change in the ratio of the power outputs. Many other similar examples are available, but have received little or no attention from the chemical point of view.

On the other hand, as is well known, chemical information of a comparative nature, which is relatively free from the effects of changing engine conditions, is provided by the ratings of fuels of different structures and by their response to antiknock compounds. Such results need not be confined to hydrocarbons of the gasoline type, but may be extended to other compounds, with possible added significance for combustion theory. An example is furnished, through the courtesy of

Heron and Gillig, by their unpublished results for a series of propyl derivatives tested as above, at 900 rpm and 212°F, alone or with 3 cc of tetraethyllead per U.S. gallon. The respective power output ratios, relative in each case to unleaded iso-octane, are as follows: *n*-propyl alcohol, 1.29 and 1.23; isopropyl alcohol, 1.54 and 1.56; 91 per cent isopropyl alcohol, 1.63 and 1.64; propylene oxide, 0.82 and 0.88; acetone, 1.72 and 1.78; di-isopropyl ether, 0.92 and 1.05. The marked lead response of the ether, and the slight response, if any, of the other substances appears chemically significant.

This brief survey shows what type of knowledge has so far been obtained regarding the mechanism of combustion in an engine. It also indicates how the complexity of the problem accounts for the scantiness of definite informa-

tion. Decided inroads are being made by the groups of investigators attacking the problem from various angles. Their realization of the difficulties encountered and of the necessary slowness of progress, coupled with their caution in drawing conclusions after each advance is made, bids fair for definite achievements and possibly for an ultimate solution of this extremely delicate and important chemical problem.

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THE COMBUSTION PROCESS IN THE DIESEL ENGINE

G. D. BOERLAGE AND J. J. BROEZE

N. V. de Bataafsche Petroleum Maatschappij, The Hague, Holland

Introduction

The Diesel engine is characterized by injection of fuel in the combustion chamber and by self-ignition. Both characteristics give rise to typical problems. The former characteristic, i.e., injection of the fuel with subsequent formation of a combustible mixture, is the fundamental one.

This mixture formation immediately preceding combustion and continuing during combustion introduces the element of heterogeneity of the mixture to an extent unknown in gasoline engines. As a matter of fact, one is faced in the Diesel engine with mixture elements varying from pure liquid globulae and deposits to fuel vapors and pure air, the condition of this heterogeneous complex changing with tremendous rapidity, due to agitation, evaporation, and combustion. As a result, conditions are always elusive; for instance, the strength of the mixture and the temperature of the flame vary continually throughout the charge.

This heterogeneity has its advantage, for it allows one to vary the load down to zero solely by regulating the fuel input, which is the cause of the excellent economy of the Diesel engine under varying load. That, however, is the only advantage. Most drawbacks of the Diesel engine do come from this very heterogeneity of the charge, the most obvious one being the impossibility of burning efficiently a quantity of fuel corresponding to the full amount of oxygen available in the cylinder, so that the power output stays behind that of an efficient gasoline engine. A second drawback, but in practice often the more important one, is the great tendency of the Diesel engine towards incomplete combustion, causing internal troubles as well as dirty and foul-smelling exhaust gases.

Figure 1 represents schematically the charge in a Diesel engine at a phase of its combustion process. Figure 2 represents schematically and comparably the charge in a gasoline engine; the difference in simplicity of conditions as compared with Fig. 1 is obvious.

This heterogeneity may be put forward as an excuse for the still existing lack of precise knowledge concerning the Diesel process, now that the Diesel engine has reached its fortieth anniversary. Whereas today the knowledge of the combustion process of the gasoline engine has developed to a point where quantitative results of general validity can be foretold, that of the Diesel engine allows only an acceptable qualitative analysis. For the first two decades the process of the

Diesel engine was only a confused picture, in which chemical and physical considerations, ignition and combustion phenomena, space and time were all mixed up. Riedler³ was one of the first to try to disentangle the various elements of the problem. He suggested the following picture of the stages of the combustion process: (1) introduction of the fuel, (2) atomization, (3) evaporation, (4) mixture formation, (5) decomposition, and (6) combustion. It is interesting to note that these stages, which Riedler visualized as being subsequent in time, actually do exist but overlap each other considerably.

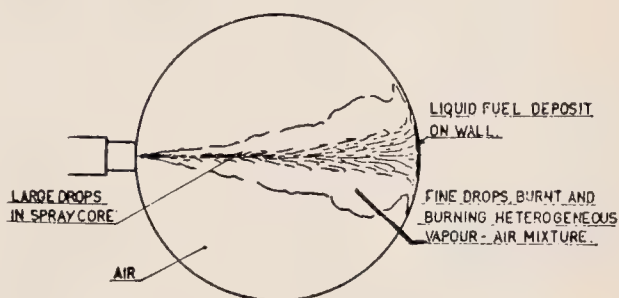


FIG. 1. Diesel engine combustion process schematized.

Before starting to analyze the Diesel process, the authors wish to make two statements: first, that for many reasons (e.g., difficulties due to the heterogeneity mentioned before) the insight available today concerning the Diesel process is due more to mechanical and physical than to chemical research. In this respect it may be useful to state that the authors, as mechanical engineers, have had the full collaboration of physical and chemical scientists; they admit, however, that it is possible that they have stressed the mechanical aspect of the problem rather much. Second, that they intend to give in this exposition only their personal views on the subject with no more than the necessary references to contradictory opinions; a fairly complete reference to the current status of research may be found in their contribution on the same subject in the recently published encyclopaedia *Science of Petroleum*.

Analysis of the Diesel Process

A. Mixture Formation

A perfectly combustible mixture is conceivable only with fuel in the vaporized state, the vapors being homogeneously mixed with the air and in such proportion that every bit of fuel and

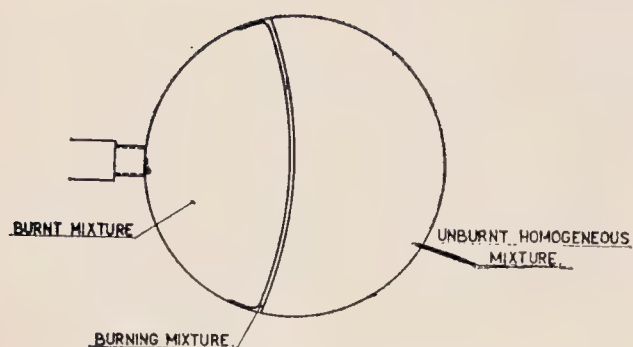


FIG. 2. Gasoline engine combustion process schematized.

oxygen can be consumed. The fact that the mixture in the Diesel engine is imperfect in all these respects adversely affects, among other things, the progress of combustion. Now combustion, to be most efficient, should occur when the piston is near its top dead center; if part of the fuel burns later, the combustion process will be the less efficient for it. Consequently, the more time in the course of combustion is taken up to correct a certain imperfection of the mixture, the more serious this imperfection is.

The mixture presents two aspects of structure: (1) Microstructure, pertaining to the size of the particles of the fuel and to whether these particles are in liquid form or vaporized, all considered locally, without regard to the condition of over-all distribution of the fuel throughout the combustion chamber; and (2) macrostructure, pertaining to the condition of over-all distribution

of the fuel throughout the combustion chamber, without regard to the size of the particles of the fuel or whether these particles are in the liquid form or are vaporized.

A good microstructure is obtained by first making drops of small sizes, which then quickly evaporate in contact with the air, with the combustion gases, or with the hot walls. In the early air-injection engines these small drops were actually formed inside the atomizer, where a blast of air of high velocity acted on the surface of the fuel fed into the air stream; only very fine drops entered the combustion chamber. In today's solid-injection engines the droplets are formed not inside the atomizer but almost entirely in the combustion chamber itself, owing to high pressure jets entering at high velocity (over 1000 m/sec) and impinging on the dense air in the chamber. (Here the name "atomizer" for the injector is actually misleading.) The mechanism of this atomization has been adequately dealt with by the National Advisory Committee for Aeronautics, by researchers at the Pennsylvania State College, and by others in very excellent pieces of research work. Figure 3, taken from Report No. 454 of the National Advisory Committee for Aeronautics, illustrates the mechanism of atomization in the clearest way.

In order to obtain small drops the injection pressure and air density should be high, the orifice of the injector small, and fuel viscosity low. As soon as the velocity of the drops relative to the air has decreased appreciably, no further

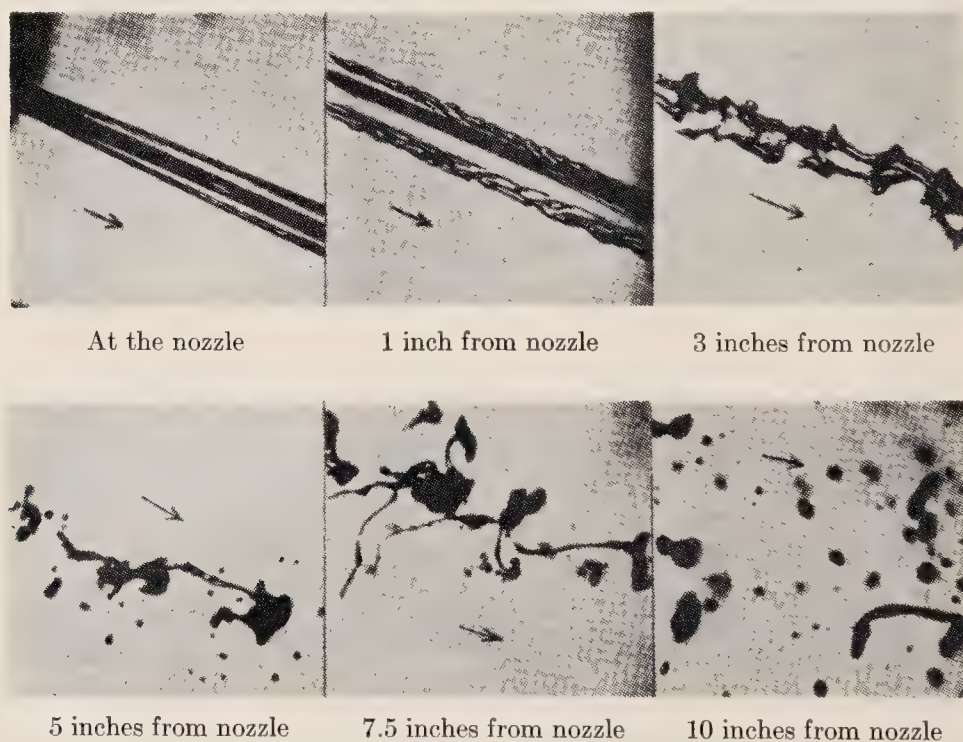


FIG. 3. Micrographs showing process of atomization (N.A.C.A.)

splitting up occurs and the next stages of preparation of the micromixture are provided for by evaporation and dispersion of the vapors in the immediate surroundings. There has been, and probably still exists, considerable divergence of opinion as to how fast droplets of the sizes considered (0.01–0.03 mm) do evaporate. Our opinion is that this process is exceedingly rapid, especially so once the combustion has set in and gas temperatures have risen from 600° to 800°C to over 2000°C. Rothrock and Waldron⁴ have shown that fuel sprays dissolve in 1 to 2 msec even before ignition; after the flame has started, a fraction of that time may be nearer the truth, which corresponds to only a few degrees “crank angle” even at an engine speed as high as 3000 rpm. In the flame, therefore, one may consider evaporation as almost instantaneous.

Spreading of the fuel vapors, as they are formed, into the wake of the droplets is effected by indiscriminate turbulence produced by the progress of the droplets through the air, and furthermore by diffusion. Though very little is known about this spreading, it seems that the reach of diffusion is small, but that its function must be important for the final molecular mixing.

In the early stages of the solid-injection engine, it had been found that the microstructure, however important, was not the biggest problem; experiments with extremely fine atomization led to disappointment. The cause of this disappointment was not clear at first, since the success of the air-injection engine had been attributed precisely to its finer atomization. As we will see further on, it was not so much the finer atomization, but the very efficient distribution (macrostructure) in the air-injection engine that caused this success. Now, with solid-injection engines, the finer the atomization, the more difficult it is to get good distribution.

Here we come to the important point of the macrostructure. The macrostructure is performed by injecting the fuel, in one or more sprays, into the air; this results in a structure as shown in Fig. 1, with great agglomerations of fuel here and pure air there. In order to get a good (i.e., homogeneous) macrostructure quickly, the relative motion between the heterogeneous portions of the charge must be increased, which explains the importance of turbulence. Turbulence, having done its part for the formation of a homogeneous macrostructure, turns over the job to diffusion again for final microstructure formation.

There exists a great diversity in the ways in which turbulence is applied in practice, for its type, energy, and origin may be vastly different; this diversity corresponds to the large variety of combustion chamber designs on the market.

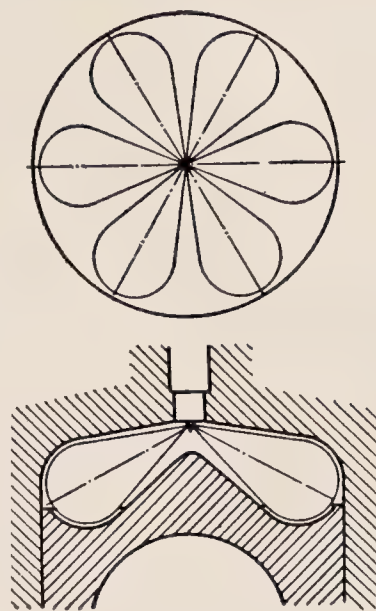


FIG. 4. Combustion chamber adapted to external shape of sprays.

The various types of air movement in combustion chambers are mainly: (a) indiscriminate turbulence, i.e., disorderly eddies with relatively small radii of gyration, which gradually disperse the clouds rich in fuel vapor; and (b) air swirl, i.e., orderly movement of the air in large orbits throughout the combustion chamber. This swirl may have two functions: the first one to “scrub” or “winnow” the fuel jets that are sprayed through the moving air, thus removing the vapors and finer drops; the second one, to act as stated above, viz., to carry parts of the charge bodily through the chamber and let indiscriminate turbulence, evaporation, diffusion, etc., finish the work in some other part. The varieties and combinations of these main types are almost endless.

Air swirls are applied, showing speeds varying from case to case, between virtually zero and a hundred or more meters per second, illustrating the range of appreciation that these swirls enjoy among designers. There are good reasons for this difference of appreciation: however useful the swirl may be to attain a good macromixture, at the same time it increases the heat transfer to the cylinder walls, and thereby the heat losses; furthermore, too fast a swirl may throw (or centrifuge) fuel out onto the walls, thus overshooting the target. Some designers, therefore, prefer to aim at good distribution by injection only, sometimes applying a swirl only as strictly required to correct insufficient distribution by the spray. They try to fit the combustion chamber around the (often only alleged) shapes of one or more sprays (cf. Fig. 4), but since distribution is so heterogeneous in a spray, they have to allow

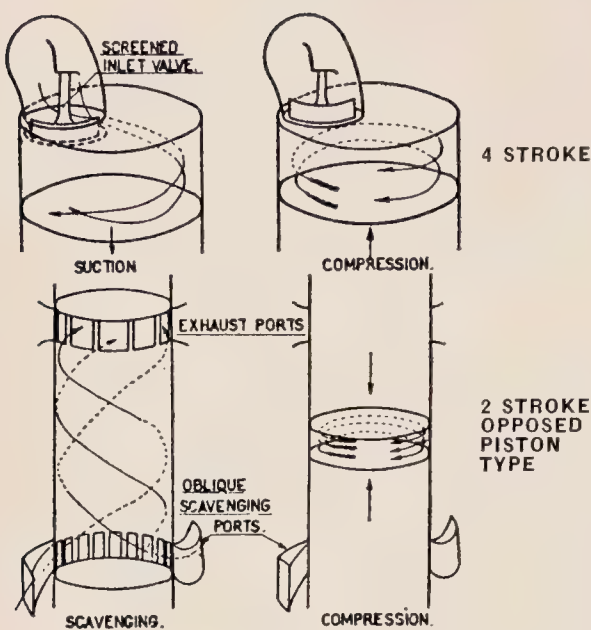


FIG. 5. Induced air movement; four-stroke and two-stroke.

for a relatively large excess of air. Although the power output is thereby restricted, the reduced heat losses may ensure a higher efficiency; thermal stress conditions of engine parts (cylinders, cover, piston) may be excellent. Of course, injection should function excellently for this design.

Other designers, though, with the idea of simplifying the functions of the injection equipment, prefer to aim at distribution by the air movement only; this solution may result in a somewhat greater reliability, a higher output, and, generally speaking, a better speed flexibility, but it involves a somewhat lower efficiency and a somewhat greater heat stress.

All kinds of compromises between these extremes exist, and usually the respective advocates of each system are most emphatic in their claims.

According to their origin, one may distinguish between induced and forced air movement. Induced air movement is such movement as is

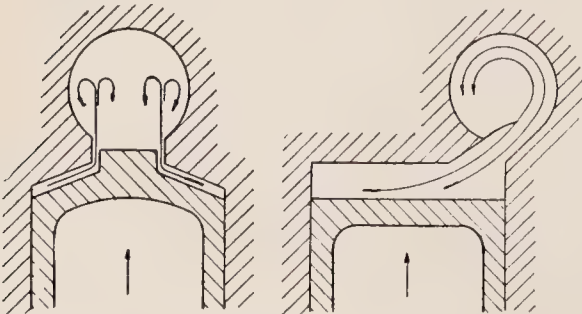


FIG. 6. Forced air movement; turbulence and swirl.

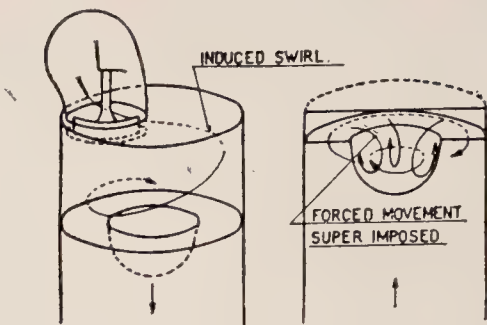


FIG. 7. Combination of induced and forced air movement.

caused by the entry of the air in the cylinder. This will always produce indiscriminate turbulence, but by means of special valves or ports orderly swirl may also be set up (see Fig. 5). Forced air movement is such movement as is caused by the transit of the air from the cylinder to the combustion chamber during compression. This may also be indiscriminate turbulence and/or swirl (cf. Fig. 6). Combination of both induced and forced air movement also exists (see Fig. 7). Finally, movement of combustion gases may be caused by the combustion itself.

The allowable velocities of induced air movement are restricted, as too high velocities would hamper the breathing of the engine; that of forced air movement is limited on account of pumping losses, yet forced air movement may be, without objection, much more intense than induced air movement. The use of either movement is limited on account of heat loss and of "fuel-throwing" ("out-centrifuging").

Movement of combustion gases as mentioned may be ensured in particular by starting combustion in a separate chamber, such as a pre-combustion chamber (cf. Fig. 8); the combustion in the prechamber causes an increase in pressure by which the gases are blown into the main chamber. Again, the design of the arrangement may be such that either indiscriminate turbulence or orderly swirl is predominant. This combustion gas movement, though very efficient in

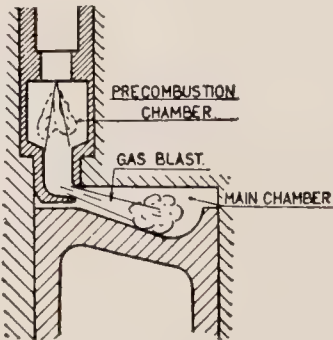


FIG. 8. Precombustion chamber principle.

many instances, is under less direct control than the two first-mentioned air movements, which depend wholly on the design, whereas the combustion gas movement depends also on the behavior of the primary combustion. Here it is the experimental work on the test bench that carries the burden of finishing the design, but it may result in a construction which performs as satisfactorily as that of the air movement type.

The winnowing action of air movement on a spray depends *inter alia* on the structure of the spray and its rate of evaporation. The spray usually consists of a core of rapidly travelling "chunks" of oil which are gradually stripped down to fine drops, and of a mantle consisting of drops so fine as to have lost their velocity. The degree and rate of atomization of the fuel influence the penetration and dispersion of a spray; the finer the droplets, the greater relatively the resistance of the air, that is, the shorter the penetration, but the greater the dispersion will be. Intense atomization makes the spray blunt or "soft," and makes it more susceptible to winnowing.

Low viscosity of the fuel as well as strong evaporation softens the spray and increases the amount of fuel removed by winnowing. The moment of ignition is therefore of great importance, since at that moment the rate of evaporation changes, as we have seen before, affecting spray softness. Therefore special study on the behavior of unignited fuel sprays will not give quantitative results that apply to real engine operating conditions; this of course greatly complicates research and development work.

Besides these considerations there remains the question of liquid fuel being deposited on the walls, either directly by the jet or by the fuel being centrifuged out by air movement. These deposits are a typical imperfection of both micro- and macrostructures. For their combustion they have to be evaporated and then distributed by air movement. In the authors' opinion the liquid deposits form one of the biggest difficulties that have to be overcome in controlling the Diesel process; this difficulty is greatest either when using low-volatility fuels such as residual fuels or with small engines (on account of the small free space for the sprays). A carefully established balance between air movement, combustion gas movement, and wall temperature is necessary to get rid of these deposits. In general, high wall temperatures are extremely useful. In some cases where the air movement is small, it may happen that evaporation is too rapid for the amount of air passing over the spot, resulting in local overrichness. Usually, a large portion of the piston crown forms part of the combustion chamber wall, and so

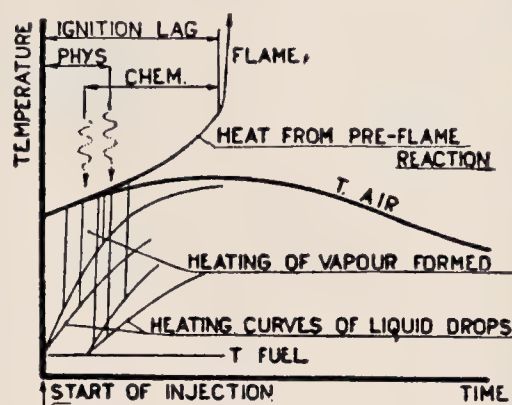


FIG. 9. Temperature during ignition.

presents a relatively high temperature (up to 600°C) right at the most important spots where the fuels jets strike. If it be required to maintain such a high temperature in small engines, one has to resort to heat-insulated linings for the combustion chamber. In the absence of these hot walls, specially adapted fuels—without low volatility fractions—would have to be used, particularly in view of good combustion at part loads.

B. Self-Ignition.

If "ignition" in the technical sense may be described as "causing flame combustion," then "self-ignition" is the process of chemical reactions in the fuel-air mixture leading to flame combustion.

In the authors' opinion the best representation of the self-ignition process in the Diesel engine is as given in a previous paper¹ from which Fig. 9 is here reproduced. The fuel, while being injected and atomized, absorbs heat from the air and evaporates rapidly. The vapors, almost instantaneously attaining the temperature of the surrounding air (which locally may drop appreciably due to this abstraction of heat, but is still of the order of 500° to 800°C), enter into chemical reactions with the air, thus leading to locally increased temperatures; finally, in one or more spots where the conditions are most favorable, flame conditions will be reached. From these spots or flame nuclei the flame may spread with great rapidity. Of course a number of flame nuclei may have been born without growing to ripeness; these would-be nuclei are overtaken by the one or two more successful ones which will start the inflammation.

The evaporation effect has been shown by the aforementioned photographs of Rothrock and Waldron.⁴ Later experiments by Selden and Spencer⁵ have shown the pressure drop due to the abstraction of heat. Large-scale pressure diagrams taken on Diesel engines may also show this pres-

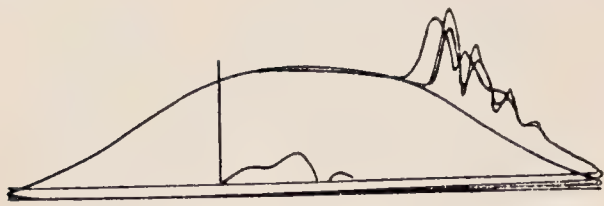


FIG. 10. Pressure drop during first part of delay.
Vertical line = beginning of injection.

sure drop, but it is soon, often even immediately, overcome by the pressure rise due to the preflame reactions (cf. Fig. 10).

The time which elapses between the beginning of fuel injection and the reaching of flame conditions (or, as others have it, the beginning of rapid pressure rise) represents the ignition delay, which the authors have subdivided into (1) "physical delay," this being the period of the development of enough fuel vapor (endothermal part) to initiate the next period, and (2) the "chemical delay," this being the period required by the preflame reactions in order to reach flame conditions (exothermal part). The physical and the chemical delays cannot, of course, be entirely separated as to time, since considerable overlapping occurs. Still, physical and chemical delays must be, principally, considered as two separate phenomena; fuels of very low volatility show much longer total delays than could possibly be explained from their chemical character alone. For fuels of normal volatility the physical delay may be very small, probably between 5 and 10 per cent of the total delay; with residual petroleum fuels and also with some vegetable oils, it may amount to some 50 per cent of the total delay, the latter being thereby almost doubled.

It has been asked just what constitutes the most favorable conditions that lead to the formation of a flame nucleus. The answer is that one can only guess. Some experiments on self-ignition of vapor-air mixtures, by Peletier and Van Hoogstraten in the laboratory with which the authors are affiliated, are very interesting. For a C.F.R. gasoline engine that was being

motored—with the ignition cut off—the investigators found that the lowest compression ratio which would cause a vaporized mixture to ignite by compression alone occurred with a mixture strength of 150 per cent of the theoretical value, and they found a similar value to hold for many fuels. This may be an indication that the flame nuclei in the Diesel engine are the spots where vapor-air mixtures of about such a composition exist; it may be assumed that fuel drops do not count in this respect.

During the same experiments (without sparks!) the heat development by preflame reactions could be clearly observed from indicator diagrams taken at a compression ratio just below the critical point (see Fig. 11); this heat development by preflame reactions was also proven by the fact that the torque required for motoring the engine would then fall off to nearly zero. The phenomenon was accompanied by luminescence and an extremely acrid smell. Approaching the critical point of self-ignition, inflammation followed gradually. Most probably that is what occurs locally and on a smaller scale in the Diesel engine in said would-be nuclei.

Having tried to grasp as far as possible the character of a flame nucleus, the further question that rises is: What is its size? Let us assume that a certain mixture strength does constitute the most favorable conditions for the formation of flame nuclei. Now, minute regions showing this very mixture strength must needs exist around every fuel droplet, since its atmosphere contains all graduations from pure fuel vapor down to pure air. If these minute regions of most favorable mixture strength, or any single one of them, were capable of acting as centers whence flame spreads with great rapidity, then ignition delay would be entirely independent of injection characteristics, turbulence, etc., but it is not. The heat losses of such minute regions may be so great that it is impossible for them to reach flame temperature in so small a space. One is led to conceive of larger and stronger nuclei, characterized by a generation of heat that surpasses the heat losses

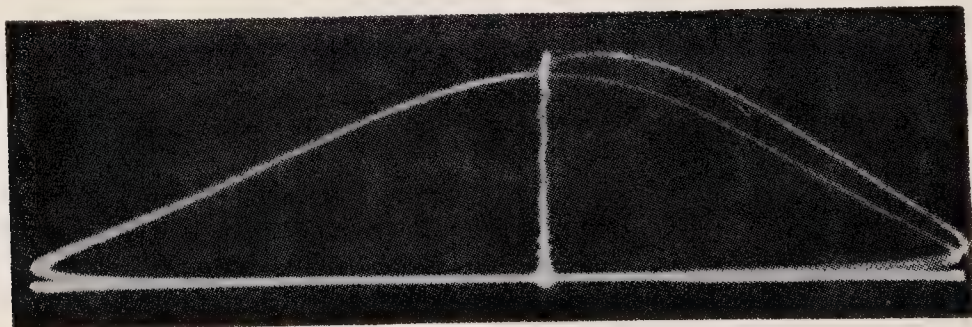


FIG. 11. Pressure developed by flameless reactions. Vertical line = top dead center position of piston.

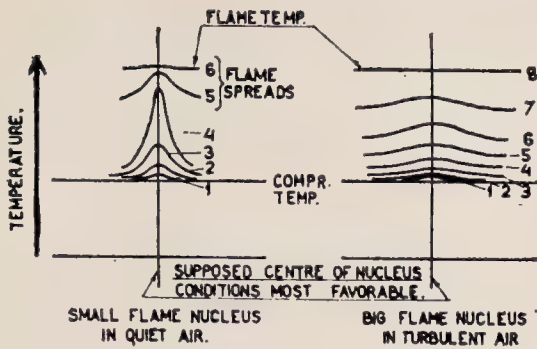


FIG. 12. Nucleus formation in quiescent and in turbulent air schematized.

to their neighborhood. The creation of these circumstances, i.e., nuclei sufficiently potent with respect to their surroundings, depends on many conditions, such as reaction velocity, temperature, and turbulence. Turbulence in particular may influence the ignition delay; this influence has been the object of many discussions and a few words about it may be of interest.

Turbulence enhances mixing and heat transfer. These combined influences affect the ignition process in different ways: first of all, they may shorten the delay, owing either to an increase

of the rate of heating of the droplets, thus shortening the physical delay, or to the compensation of a locally too large heat abstraction from the air, thus shortening the chemical delay. Therefore, in its first aspect, turbulence acts beneficially on the delay. In its second aspect, however, the combined influences of turbulence tend to lengthen the delay: as soon as the local mixture temperatures exceed the temperature of the surroundings the greater heat transfer tends to cool the would-be nuclei. The mixing influence, moreover, tends to decrease the local vapor-air ratio, which at first has no effect at all, as long as there still remain regions very rich in vapor; but as soon as these have been dispersed, the mixture becomes diluted below the composition most favorable for self-ignition. Thus with strong turbulence both the increased heat transfer from the nuclei and this dilution of regions rich in vapor may lead to increased delays. Schematically these favorable and unfavorable influences may be illustrated by Fig. 12. Under favorable influences a nucleus may be, so to speak, of the size of a mere pinhead; the pressure diagram will deviate only very little from a straight compression diagram, up to the moment where pressure begins to rise rapidly (cf. Fig. 13),

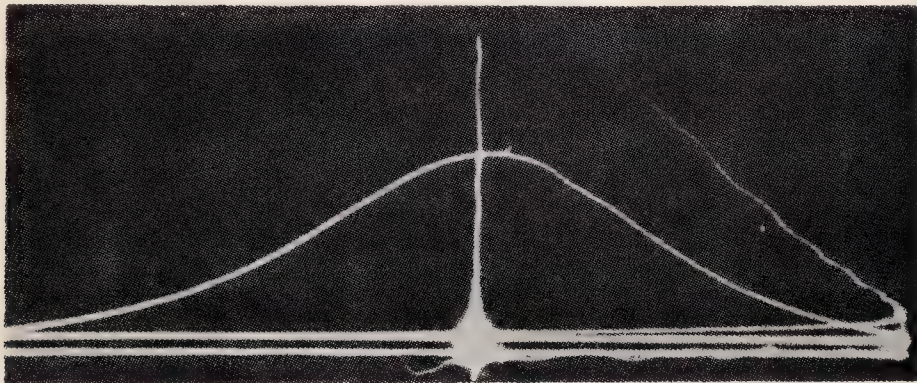


FIG. 13. Diagram of combustion starting from a small nucleus (moderate turbulence). Vertical line = top dead center position of piston.

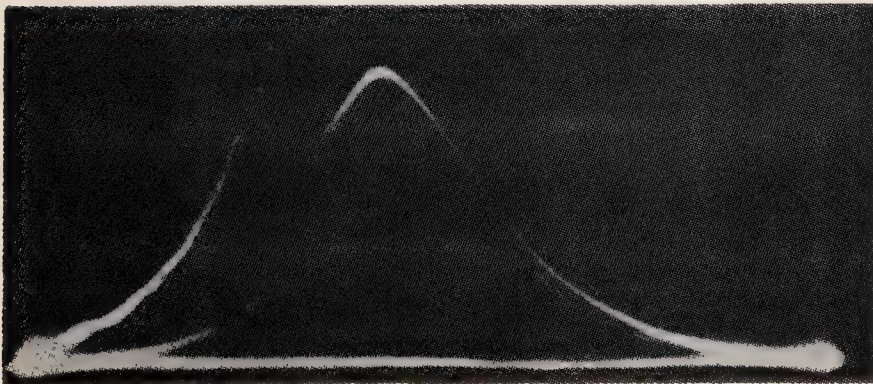


FIG. 14. Diagram of combustion starting from a big nucleus (high turbulence). reading from right to left.

— BLAST AIR PRESSURE : 60 ATM.
 --- BLAST AIR PRESSURE : 45 ATM.

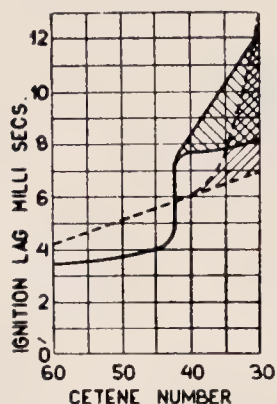


FIG. 15. Delays in air-injection engine.

owing to combustion; under unfavorable influences there may be formed a nucleus of much larger dimensions (cf. Fig. 12); a gradual extra pressure rise of several atmospheres may have been produced by preflame reactions in a large portion of the charge, before, finally, combustion proceeds rapidly (cf. Fig. 14). (The two diagrams shown on Figs. 13 and 14 are taken on a

low-turbulence and a high-turbulence type of engine, respectively.) The following experiments on an air-injection engine appear to show both favorable and unfavorable influences of turbulence (Fig. 15), low blast air pressure (45 atm) giving low turbulence, and higher blast air pressure (60 atm) giving higher turbulence. For cetene numbers from 60 to 42, the higher turbulence gives shorter delays than the lower turbulence; between 42 and 30, however, the influence is just the reverse. (The cross-hatched area in Fig. 15 is due to unstable ignition conditions.)

After having shown the influence of turbulence in dispersing regions rich in fuel vapor and the possible effects therefrom on ignition delay, we shall now briefly discuss some further effects on the rate of burning. Figure 16 shows how turbulence affects, through the rate of burning, the shape of the pressure diagram of a given engine (which was equipped for either air injection or solid injection) for different loads, that is, for different fuel-air ratios. It will be seen that when using air injection the rate of burning drops appreciably with the load, which is due to increasing leanness of the mixture. When using solid injection, on the other hand, and for about

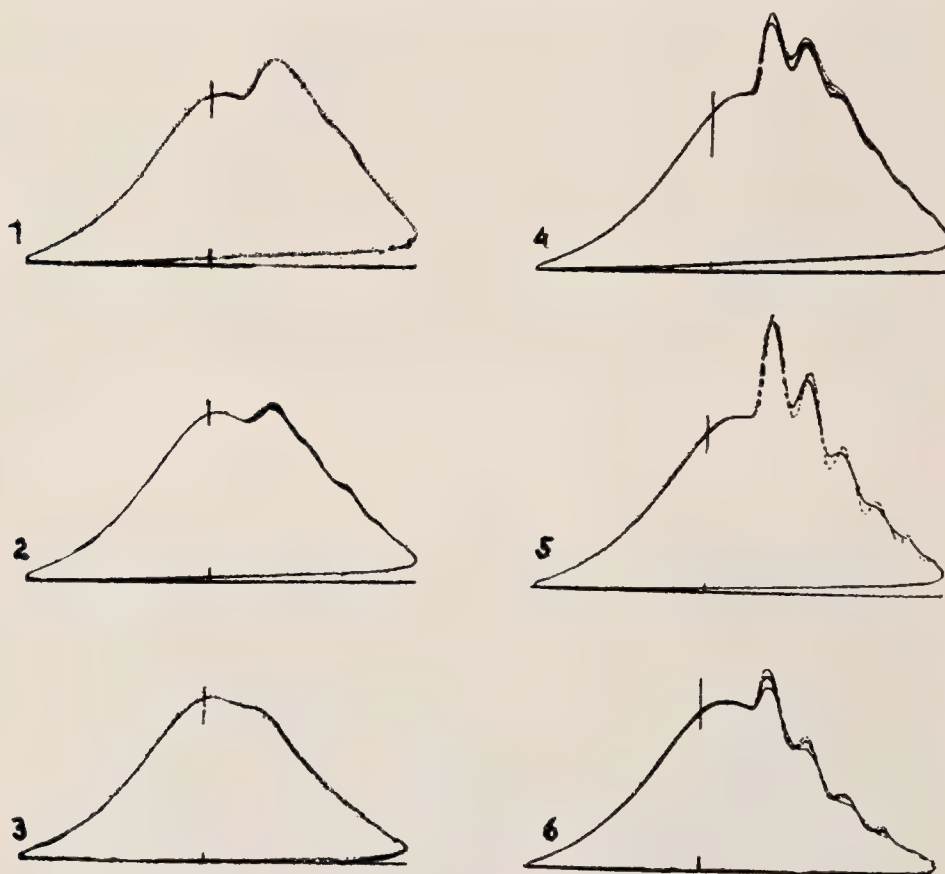


FIG. 16. Diagrams showing decrease in combustion velocity with decreasing load in air-injection engine (1, 2, 3) and high combustion velocities in solid-injection engine (4, 5, 6). The short vertical lines show the beginning of injection.

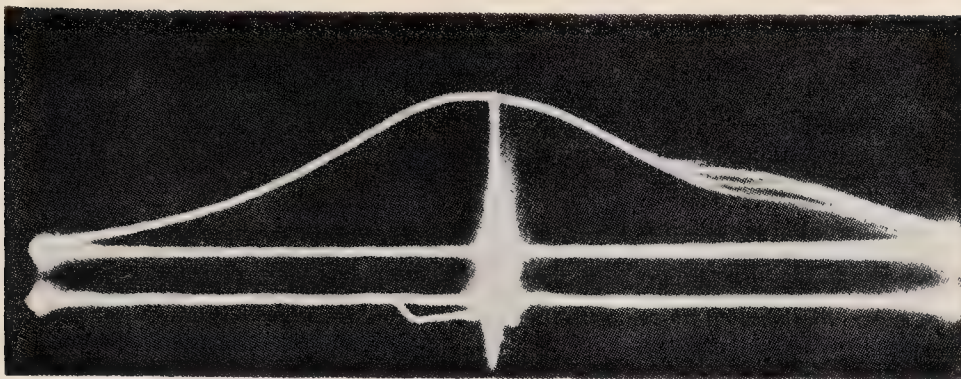


FIG. 17. Effect of extremely long delay in solid-injection engine.

the same delay values, the rate of burning is better maintained when the load is decreased, which is due to the more localized fuel distribution through the charge. Of course, in the solid-injection engine also the rate of burning may eventually become insufficient, due to the delay becoming extremely long, as shown in Fig. 17. One must keep in mind the hypothetical character of the above-mentioned considerations; the ways and means of direct observation, which would give better evidence, fail at present.

Such is also the case when it comes to an investigation of the chemical side of ignition. The ignition process is short (0.001 to 0.005 sec), and as most chemical hypotheses have been derived from experiments made under conditions entirely different from the actual process, it always has to be proved over again that the conclusions hold good. The three main hypotheses are the following: (1) fuel molecules combine with oxygen directly (oxidation theory); (2) fuel molecules form unstable peroxides which decompose exothermally (peroxide theory); (3) fuel molecules tend to crack and become thereby abnormally sensitive to oxygen; or they do crack and oxygen reacts with the free radicals *in statu nascendi* (thermal stability theory).

Regarding the oxidation theory, there is no definite proof that fuel and oxygen do not react directly with each other, perhaps following some kind of chain reactions. True, in an oxidation test the affinity of the fuel for oxygen is smaller than the actual delay period would indicate; however, conditions in an oxidation test are entirely different from those in the actual engine process, and the former cannot be considered, therefore, to furnish definite proof of what happens in the latter. For instance, by extraction with sulfur dioxide those fractions of a lubricating oil are removed which, in the crankcase, are most prone to oxidation; yet the original oil, being lower in cetene number than the raffinate, is less prone to ignition in the combustion chamber. Here again, conditions obviously are vastly

different. A further example is the fact that, although carbon disulfide is known to combine eagerly with oxygen at temperatures materially lower than prevail in the combustion chamber, yet this very carbon disulfide, when blended with a fuel, will lower its cetene number, that is, its eagerness to combine with oxygen.

As to the peroxide theory, initiated by Tausz and Schulte,⁶ the presence of peroxides has repeatedly been proved during flameless reaction experiments; yet exothermal decomposition of these peroxides does not seem to occur, since, as we have seen, the development of the flame in the engine hardly has the character of a phenomenon initiated by an explosive exothermal reaction such as Tausz and Schulte supposed, but is a gradual building up of a heat center. Peroxides are known as ignition inducers; the authors have experimented with organic peroxide dopes in the fuels and also with ozonides formed in various fuels by ozone treatment. These experiments have rather led to the conclusion that both peroxides and ozonides may act as carriers of active oxygen, enriching the air in the engine with small quantities of such active oxygen; this has an effect similar to either an increased temperature or an increased oxygen content, both shortening the delay. One might imagine that the tendency of a fuel to form peroxides, ozonides, or other unstable oxygen compounds would concur with its cetene number. Such a concurrence has not been confirmed by the following experimental facts: As for peroxides, tetrahydronaphthalene does develop at temperatures up to 100°C a peroxide which is a powerful dope, yet tetrahydronaphthalene without peroxide has an extremely low cetene number. As for ozonides, experiments with fuels subjected to ozone treatment before being used in the engine showed that, without any connection with the cetene number of the original fuel, some fuels did increase in cetene number, while others did not (see Table I).

Whereas these considerations do not show that

TABLE I

Effect of ozonization upon the cetene number of a fuel

Fuel	Cetene numbers	
	Before ozonizing	After ozonizing
A	51	70
B	49	52
C	44	70
D	44	44
E	40	46
F	40	40

these particular peroxides or unstable oxygen compounds have a part in the process unless administered beforehand to the fuel, of course other peroxides may be generated, under engine conditions, that do influence the process. The thermal stability theory, advanced by Prof. Dr. W. J. D. van Dijk and the authors, suggests that the tendency to ignite is mainly the result of the thermal unrest of the fuel molecules. One of the starting points for this hypothesis was the high degree of agreement between two formulas, one evolved by us for the evaluation of ignition quality in the engine, the other by A. Holmes for the evaluation of gas-making properties of a gas oil. Experiments on the initial rate of cracking appeared to sustain the hypothesis that a higher ignition quality corresponds to a high initial rate of cracking. Isooctane was an exception in this respect, in that it showed a very high initial rate of cracking notwithstanding its low ignition quality; this could be explained by means of Rice's observation on the relative inactivity of the isobutyl group, which would be the radical split off by isooctane. Later experiments in the authors' laboratory with compression of hydrocarbon-nitrogen mixtures in an engine (with the exclusion of oxygen, in order to prevent oxidation) have shown, however, that at temperatures corresponding to those in the engine, little or no decomposition takes place, unless some oxygen is present. This seems to strengthen that part of the hypothesis mentioned above which states that "fuel molecules tend to crack and become therefore abnormally sensitive to oxygen."

So far, no more information has been obtained, and the problem of the chemistry of self-ignition in the Diesel engine is still unsolved. Cooperation with the investigators of gasoline detonation appears to be indicated. Of such cooperation the compression experiments mentioned above are an

example; the close relationship between cetene and octane numbers is also well known.

C. Combustion Stages

In principle, four combustion stages may be distinguished, as seen from Fig. 18, which shows, by means of a schematic pressure diagram, the following combustion stages: (1) delay; (2) inflammation of the fuel present at that moment; (3) injection-controlled combustion—burning of fuel injected into the flame; and (4) afterburning of all the fuel that has not yet found its oxygen or of which the burning rate had been too low (weak mixture, chilling).

Comparison with the ideal diagram, also given in Fig. 18, where every bit of fuel would be burned immediately as it enters the combustion chamber, reveals that there are mainly two independent causes for combustion lagging behind: namely, the delay and the afterburning, the former being caused through deficiency of reaction velocity, the latter mainly through deficiency of mixing. All variations on the schematic diagram are met with in practice.

D. Physical and Chemical Aspects of Combustion

1. *Physical Aspects.* The purpose of combustion in the engine is the development of pressure, and the characteristics of the pressure diagram form the principal physical aspect of combustion. Two requirements should be taken into account: (1) The development of pressure should occur as near the top dead center position of the piston as possible, having due regard to a reasonable maximum pressure. (2) The shape of the combustion pressure curve should be as smooth as possible, so as not to cause vibrations of the engine parts ("Diesel knock"). The control of the development of pressure would be entirely in the hands of the designer if the ideal diagram of Fig. 18 could be realized, the maximum

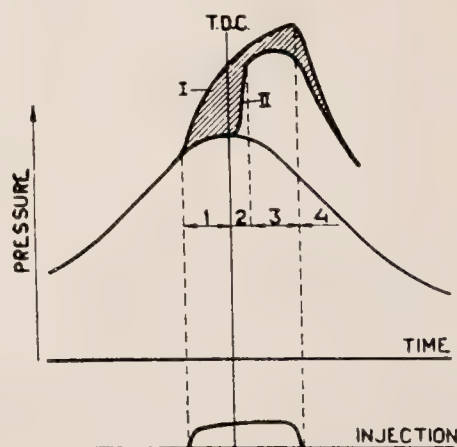


FIG. 18. Actual and ideal pressure diagrams.

pressure being controlled by suitable timing of the injection. Actually this is still the method of controlling the maximum pressure, but as the course of combustion depends *inter alia* on the type of fuel (viscosity, ignition quality, volatility) the maximum pressure may also vary with the fuel used, e.g., to the extent of 1–5 atm.

In order to develop the pressure as near as possible to the top dead center, afterburning must be reduced to a minimum. It may be said that wherever fuel and air have been mixed in a proper ratio so that a high flame temperature is reached, the reaction velocity is high enough to satisfy the requirements as to restriction of afterburning for the highest engine speeds. The causes of afterburning, which have been mentioned above, may be summed up as follows:

(1) *Inefficient mixing, in particular overrichness of parts of the charge.* This tends of course to become the worse the greater the quantity of fuel, but it depends fundamentally on engine design. The influence of fuel quantity (load, brake mean effective pressure) is seen in Fig. 19, showing how combustion becomes more and more prolonged with greater loads. Consequently, the specific fuel consumption increases with the load. This is clearly shown by curves of fuel consumption per indicated horsepower-hour, i.e., per unit of work done in the cylinder. (The consumption per brake horsepower-hour increases also for lower loads, but this is due to the decreasing mechanical efficiency (cf. Fig. 20) and not so much to afterburning.)

(2) *Deposits of liquid fuel on the walls of the combustion chamber.* This phenomenon is illustrated very well in Fig. 21, showing a photograph from N.A.C.A. Report No. 545 by Rothrock and Waldron.⁴ At the spots where the fuel jets strike the walls, flames are seen to linger after the main combustion is finished. This happened especially in the low load zone (air-fuel ratio 25.7 to 94). Under higher loads the phenomenon became less

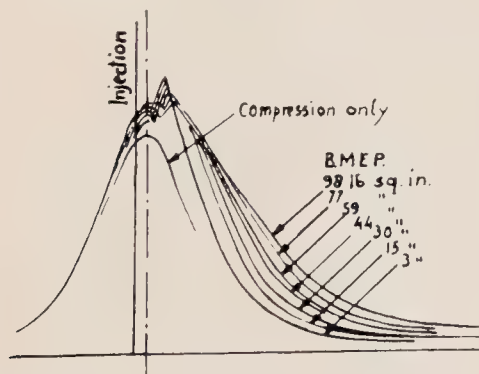


FIG. 19. Diagram showing increased after-burning with increased load (Dicksee).

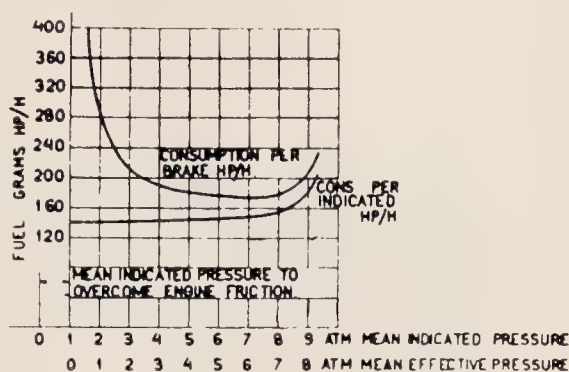


FIG. 20. Typical fuel consumption curves.

clear, since then there were more causes provoking afterburning; with extremely small fuel quantities the sprays did not reach far enough to touch the walls. In practice, similar zones of joint load condition and afterburning due to fuel deposits may exist; it depends on numerous circumstances whether the trouble will be bad at all and if so, at which load. It usually will be more pronounced at the lower end of the load range, due to poorer heat conditions and to longer delays, and especially due to the low rate of evaporation. It is certain, however, that with heavy residual fuels it persists often over the entire load range and results then in a higher over-all fuel consumption and a lower maximum power.

(3) *Long delays during which the fuel mixture has become lean throughout, resulting in low flame temperatures* (cf. Fig. 17).

Further there are still a few chemical causes:

(4) *Dissociation of the flame gases, especially at high loads, reducing the maximum flame temperature.* The degree to which this phenomenon participates in causing afterburning may be estimated as small in comparison with the phenomena mentioned above.

(5) *Chilling of the flame near cool walls.* This will mostly accompany the second and third causes mentioned and would probably be quantitatively far less serious, but for the secondary phenomenon—that of leaving partially burnt products, which may accumulate in the engine.

Of course, on first inspection of an engine and of its diagrams, it is not obvious which cause of afterburning prevails. Often experiments with fuels of different types may throw more light on the matter.

From the foregoing it is evident that a fuel of low viscosity, high volatility, and high ignition quality will ignite easily but will tend to form localized overrich mixtures. High viscosity, low volatility, and low ignition quality will, on the

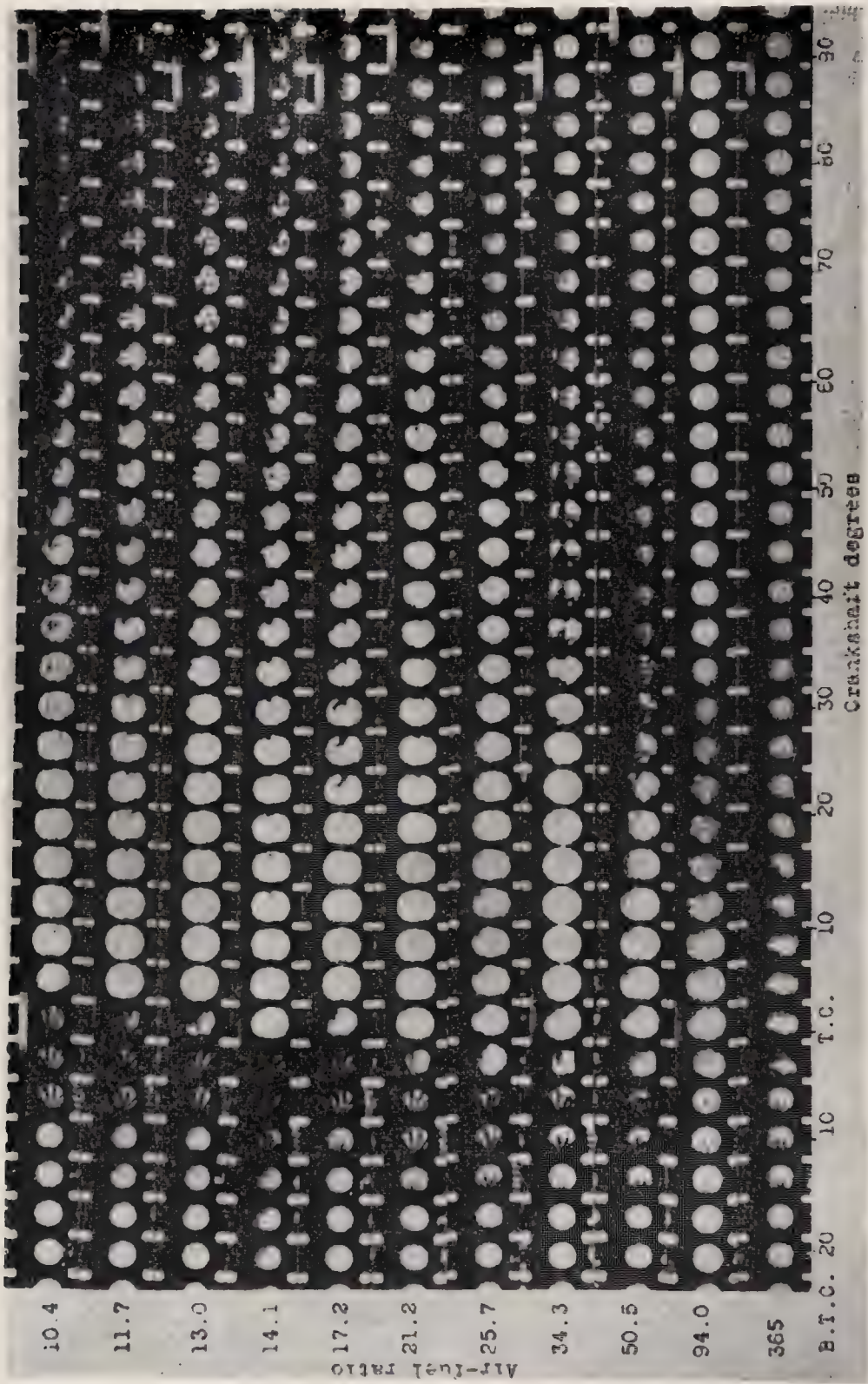


FIG. 21. Photographs showing afterburning due to fuel deposits on combustion chamber walls at air-fuel ratio between 94.0 and 25.7 (N.A.C.A.).

other hand, cause a fuel to aggravate wall deposits and to form well-distributed mixtures, which may, due to this good distribution, become too weak for rapid burning. The effect of a change of fuel on the efficiency of combustion may thus give some indication as to the most obvious cause for afterburning. Quite often, though, the various causes are so nicely balanced that the change of fuel has little effect; this does not imply at all that the engine is perfect. An analysis of the composition of the partially burnt products may then be useful.

The shape of the pressure diagram is evidently greatly influenced by the delay. The delay, followed by the subsequent inflammation, tends to give rise to one or two kinks in the pressure rise, where the rate of the pressure rise may change so abruptly as to cause vibration (audible as Diesel knock) and increased stresses in engine parts. In a given engine the knock will usually increase with the delay, then decrease again (cf. Fig. 22). The increase is due to the increase of the fuel quantities liable to explode with the delay and to the steadily improving distribution of the mixture; the decrease is due partly to the final weakening of the mixture which always occurs, and partly to the rapidly increasing volume of

the combustion space. The state of turbulence during the inflammation period appears to have much to do with the rate of pressure rise, but whether this is due to improved mixing or to more rapid flame propagation cannot be made out. What the rate of pressure rise will be for a certain delay depends entirely on engine type, load, and speed (cf. Fig. 16). Thus some engines may have either short or long delays and yet remain smooth (cf. Fig. 23), whereas others will have a much more pronounced tendency to knock (cf. Figs. 13, 14). Therefore, although generally speaking a fuel of high ignition quality may decrease objectionable knocking in many engines in comparison to a fuel of low ignition quality, in other cases the effect may be less pronounced, and in still others neither of them will knock in an objectionable way.

2. Chemical Aspects. The chemistry of the complex combustion occurring in a Diesel engine is far from being entirely known. The following material, which includes much of a paper presented last year,¹ may be advanced as a crude outline of the general situation. Combustion of hydrocarbons may be, in principle, a direct oxidation (for instance, hydroxylation according

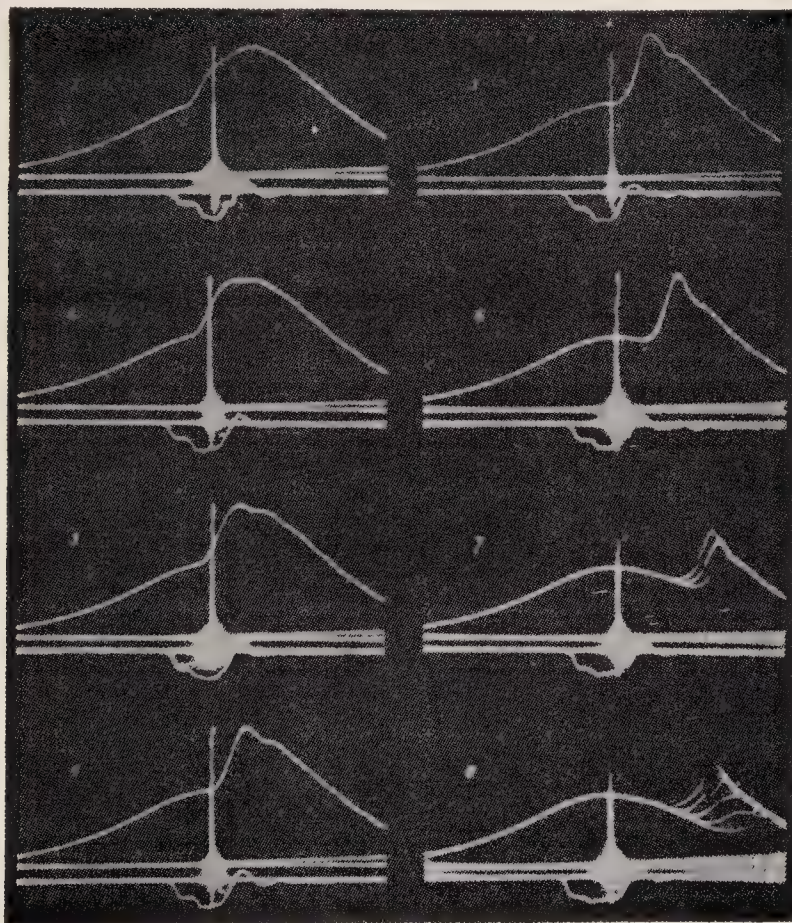


FIG. 22. Series of diagrams with increasing delays (1 to 8).

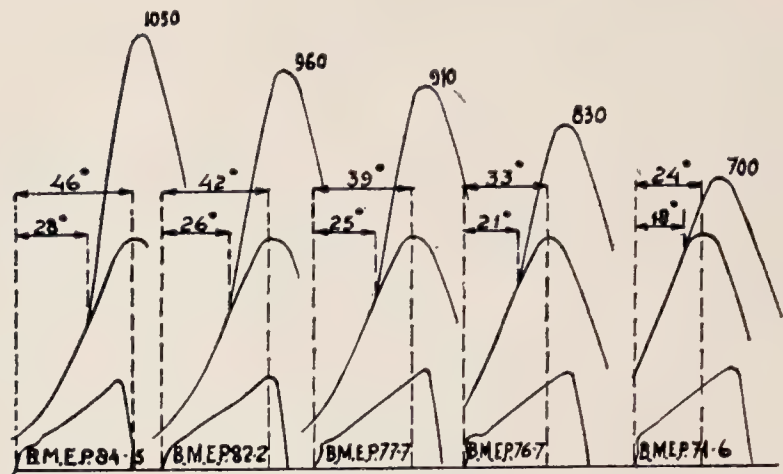


FIG. 23. Smooth pressure rise notwithstanding long delays.

to Bone and Wheeler) or a decomposition followed by oxidation of the destruction products (Aufhäuser's theory of destructive combustion). Haslam and Russell² came to the practical conclusion that generally both types of processes will occur side by side. When the fuel has been vaporized and well mixed with air before burning, the first type of reaction is most likely to develop, but when fuel vapor is suddenly exposed to high temperatures before mixing, the second type of reaction prevails. The conditions for the first type of reaction are met with in dry mixtures in gasoline engines, but in the Diesel engines there appears to be no doubt as to the condition being more favorable for destructive combustion; the liquid fuel drops surrounded by flames form as many centers of vapor development, whereas the mixing process comes only afterwards. The characteristics of the direct oxidation process in mixtures of normal air-fuel ratio are as follows: blue flame (carbon dioxide and carbon monoxide radiation), no tendency to soot either from overrichness or from chilling, but production of carbon monoxide, aldehydes, and acids under chilling conditions. Characteristics of the destructive combustion process are as follows: radiant yellow-white flame ($C=C$ or black body radiation), and tendency to soot when locally overrich and when chilled. Under overrich conditions carbon monoxide and hydrogen are formed by either process.

The evidence given by photographs of the flames, by exhaust color on overload, and by contamination of lubrication oil by soot, all point to destructive combustion as being predominant. Acrid exhaust odors, formation of carbon monoxide at low loads (see Fig. 24), and varnishlike deposits on pistons and in lubricating oil point to direct oxidation as part of the process, and are most noticeable under light loads and with long delays. This proves without

further detail that actually both processes go on side by side.

Chilling, due to cool walls, and dissociation (mainly of carbon dioxide) at high temperatures have been briefly mentioned as chemical causes of afterburning. When it is considered that a severe degree of contamination may be caused by incomplete combustion, due to chilling, of only a very small percentage of the fuel, it is obvious that the incomplete combustion of so little fuel will not materially affect the efficiency of the cycle.

From the foregoing, it is seen that analysis of the products of incomplete combustion may be a guide towards a better understanding of the Diesel process. From a practical point of view these products hold one of the biggest problems in Diesel engine development.

Acrid smell and blue fumes from unburnt fuel are intolerable in road vehicles. It has been shown in a practical way that engine design may overcome them by allowing no fuel in the liquid state

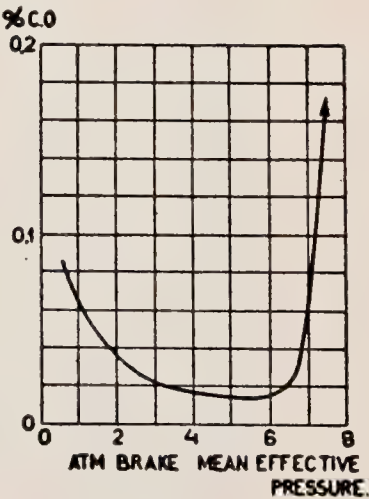


FIG. 24. Carbon monoxide content of exhaust gases.

to come into contact with cool walls. Carbon monoxide is still more intolerable, but as the carbon monoxide content in Diesel exhaust gases is much lower than in gasoline exhaust gases, and as the latter generally are unobjectionable from a hygienic point of view, this is still more true in the case of the Diesel engine. A further effect of liquid fuel deposits may be carbonization, especially with residual fuels, leading to piston and valve troubles. Varnishlike deposits in quantities that will cause sticking of the piston rings within a short time are seldom encountered, but their influence at continuous operation may be severe enough, even if this influence be only the forming of binding material in crankcase sludge.

Stationary and marine engines usually have to be rated, on account of heat stresses, to low outputs, so that their exhausts may always be clear. In the case of vehicle engines, maximum output being required, the formation of soot limits the output, not only with regard to at-

mospheric conditions in the streets, but also because of the blotting paper action of the soot in drying up the cylinder walls, thus leading to piston troubles. Soot, furthermore, constitutes the greater part of the lubricating oil contamination.

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Discussion

A. M. ROTHROCK: Mr. Boerlage and Mr. Broeze are to be congratulated on their comprehensive survey of the combustion process in the Diesel engine. They have presented a clear analysis of their own and other researches. Papers presenting such an analysis are particularly valuable in that they permit general conclusions to be drawn from a mass of research and so prevent us from drawing erroneous conclusions from single researches.

In the third paragraph of the paper the authors state that the heterogeneity of the mixture in the engine permits the load to be varied down to zero solely by regulating the fuel input. Although we know, as shown by Fig. 21, that stratification of the charge does occur at low loads, we cannot be sure that in the Diesel engine such stratification is necessary. Gaseous combustion tests have shown that as the temperature of the gas is increased the limits of inflammability are also increased. With the ambient air at a temperature sufficient to cause the fuel to ignite in 0.001 sec or less, the number of ignition sources is infinite, so that each fuel droplet on vaporizing may act entirely independently of the surrounding droplets in the case of extremely lean but uniform mixtures. I also question that the excellent economy of the Diesel engine at part loads is caused by the fact that the fuel only is regulated; rather the economy at light loads is the economy inherent in the high compression ratio used with the Diesel, and at full load the good economy is really poor economy if based on what the cycle is capable of delivering providing all the fuel is burned early in the expansion stroke.

Our inability, so far, to provide means for efficiently burning a quantity of fuel corresponding to the full amount of oxygen available in the cylinder prevents us from obtaining the economy inherent in the high compression ratio of the Diesel engine, but recent researches show that the power output may very closely, if not actually, equal the power output of a spark-ignition engine. With a normally aspirated engine, as shown in Fig. 14 of the paper presented by Dr. Selden and myself, an indicated mean effective pressure of 163 psi was obtained. This value corresponds to that obtained at a compression ratio of between 7.5 and 8.5 on a spark-ignition engine.

The authors' remarks on the slowness of fuel vapor diffusion are particularly important. It seems to me that this physical fact presents the chief obstacle to be overcome in the development of the high-speed Diesel. Also, I agree with them fully in their statement that increased atomization will not necessarily improve engine performance. Their discussion on microstructure and macrostructure is particularly worthwhile. However, I would sooner use the terms "atomization" and "vaporization" than "microstructure," and the term "distribution" rather than "macrostructure."

In the photographic researches on combustion conducted by the National Advisory Committee for Aeronautics, we have never obtained any evidence of the high air velocities centrifuging the fuel to the outside of the chamber. Our researches indicate that it is extremely difficult to obtain a good mixture either by air flow alone or by nozzle design

alone, but that the two means must supplement each other if the best performance is to be obtained. I also question the statement that greater flexibility is obtained with the use of air flow. We have idled an engine with a quiescent combustion chamber at 200 rpm. Our tests indicate that the difficulty in idling an engine without air flow can be overcome through the correct design of the injection system. Air flow definitely permits greater power output and lower fuel consumption to be obtained, particularly at high speeds.

In connection with the authors' statement that forced air movement may be much more intense than induced air movement, I would like to add that in our tests on the N.A.C.A. combustion apparatus we have found that the induced air movement obtained unintentionally may be such as almost to destroy the forced air movement. Consequently particular care must be taken in the engine design so that the induced air movement will not oppose the forced air movement.

Our tests indicate that the penetration of the spray is probably less dependent on the atomization than on the closeness of the drops in the atomized jet. As was shown by Kuehn (Atomization of Liquid Fuels, Natl. Advisory Comm. Aeronaut. Tech. Mem. No. 331, 1935; translated from *Der Motorwagen*, Dec. 10, 1934, Jan. 20, 1935, Feb. 10, 1935), even the largest drops would not penetrate through the air in the combustion chamber more than a fraction of an inch unless they were sufficiently close to entrain the air within the spray.

It is questionable whether or not we should place so much emphasis on flame. Whether or not a flame nucleus is formed depends on our definition of flame. Webster's dictionary defines flame as "a body of burning gas or vapor." In their paper, I presume that Mr. Boerlage and Mr. Broeze are referring to a

luminous flame nucleus. If heat is being generated through the chemical reaction in the combustion chamber, the mixture is burning and we have combustion, even though we do not necessarily have luminous flame. In any case, the luminosity is simply an indication of the temperature and constituents of the gas at the instant under consideration and has no direct relationship to the rate of pressure rise in the combustion chamber. In our own tests (A. M. Rothrock and C. D. Waldron: Natl. Advisory Comm. Aeronaut. Tech. Rept. No. 525, 1935) we have recorded appreciable pressure rise before recording luminescence. But it must be further remembered that flame which is visible to the eye may or may not be recorded on the photographic film used in the tests, and that certain photographic films will record radiations that are not visible to the eye. Along this same line of discussion, the recent researches of Wilson and Rose [SAE Journal 41, 343 (1937)] offer additional information on the relationship between the start of radiation from the combustible mixture and the start of combustion pressure rise. When the motion pictures obtained by Rothrock and Waldron (see reference above) are projected they show various luminous combustion nuclei appearing and disappearing when the start of injection was 60° before top center. With the later injection starts, all the visible nuclei spread or merged into large combustion areas. I think a too detailed discussion of the process by which these nuclei are formed should wait until we have more information than is available at present.

The authors' statement that a mixture strength of 160 per cent of the theoretical autoignited at the lowest compression ratio is particularly interesting. This fact may have a direct bearing on the long afterburning period in the Diesel engine by requiring an overrich mixture in parts of the combustion chamber to initiate combustion.

FACTORS CONTROLLING DIESEL ENGINE PERFORMANCE

A. M. ROTHROCK AND R. F. SELDEN

National Advisory Committee for Aeronautics, Langley Field, Virginia

Introduction

The performance of any internal-combustion engine, irrespective of its operating cycle, is primarily a function of the thermal energy liberated per cycle, the part of the cycle in which it is liberated, the compression ratio, and the mechanical limitations imposed by the engine structure. For the purpose of this paper, engine performance is determined by two quantities: first, the highest indicated mean effective pressure (i.m.e.p.) attainable, and second, the minimum fuel consumption expressed as pounds per indicated horsepower-hour. In order to secure optimum values for these quantities it is necessary that the combustion be completed as early in the power stroke as possible, with the provision that neither the explosion pressure nor the rate of pressure rise shall exceed certain limiting values.

The combustion in a compression-ignition or Diesel engine differs from that in a spark-ignition engine in that a large portion of the fuel must be mixed with air during the combustion period. The Diesel engine must be a compromise between extensive mixing before combustion, with its attendant early efficient burning but excessive rate of pressure rise, and limited mixing before combustion, giving a permissible rate of rise but a lower thermal efficiency. Provision must therefore be made for supplementary mixing of the major portion of the fuel charge with the available air after ignition by a proper coordination of the injection system, the combustion chamber, and directed air flow. It is the purpose of this paper to outline the influence of these factors on combustion in Diesel engines as revealed by a number of investigations conducted for the National Advisory Committee for Aeronautics (N.A.C.A.) on injection systems, combustion chamber design, and engine operating conditions, and to show how these factors control engine performance.

Operation of Typical Injection Systems

The fuel for most modern high-speed Diesel engines is injected, as a liquid under high pressure, through one or more small orifices directly into the combustion space of each cylinder by means of a displacement pump connected to an injection valve by a tube of appropriate dimensions. Each of the individual parts of such a system should be designed and coordinated to fulfill the following conditions: small variation in

timing and fuel quantity from cycle to cycle; proper spray penetration and distribution for the particular combustion space; a sharp but controllable spray cut-off for various load conditions; and perhaps some control of injection rate and start of injection if the engine is intended to operate efficiently over a great speed range.

The plain, pintle, multiple-orifice, and two-impinging-jets nozzles are representative of the many different nozzle styles used in commercial engines. Such nozzles are classified as open or closed, depending upon whether or not the

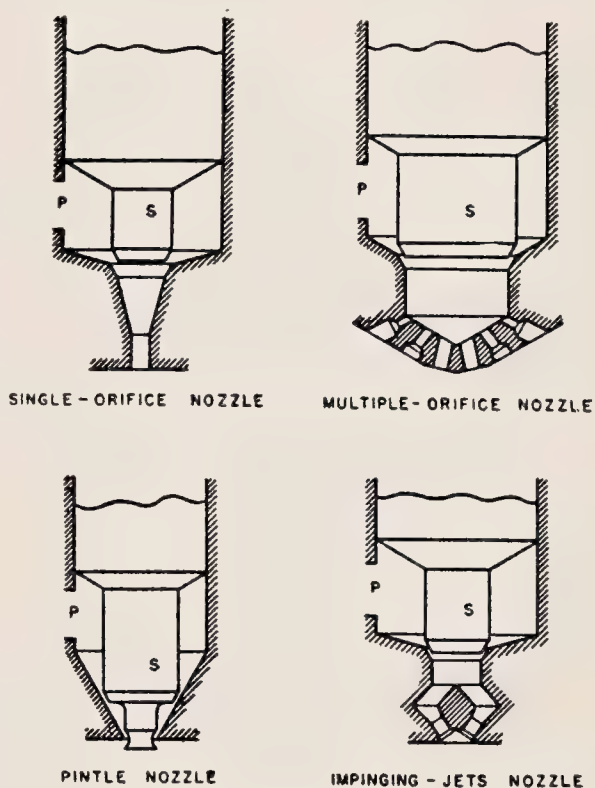


FIG. 1. Typical closed injection nozzles.

cylinder gas has access after spray cut-off to an appreciable passage length above the flow-restricting orifice section of the nozzle. The nozzles sketched in Fig. 1 are all of the closed type with the valve stem *S* shown in the raised or injection position. If the oil pressure in the passage *P* falls sufficiently, a suitable spring above the valve stem forces the latter down until its seating surface is in contact with a corresponding surface on the nozzle, thus providing a gas-tight seal between the cylinder interior and the fuel passage above the nozzle.

The purpose of the nozzle is twofold—to distribute the fuel throughout the combustion

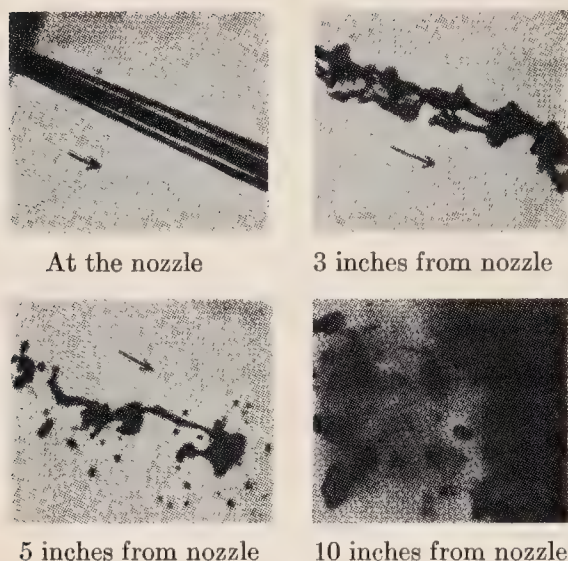


FIG. 2. Distintegration of low-velocity jet in atmospheric air. Injection pressure = 100 psi.

chamber and to assist in breaking up the fuel jet into the numerous droplets necessary for the intimate mixing of the fuel and air. Disturbances of the fuel jet as it issues from the nozzle produce surface irregularities that are drawn out into fine ligaments by the relative motion of the fuel and air. The liquid in each ligament, after detachment from the main jet, quickly contracts into a spherical droplet by the action of surface tension. This process is illustrated in Fig. 2 for a low jet velocity.⁸ Figure 3 is a photomicrograph of the impressions made by such drops after settling upon a lampblack surface.⁵ A detailed analysis of the size distribution of these impressions corresponding to various injection pressures (or jet velocities) furnished the data for the curves in Fig. 4. The percentage of fuel in each group was based upon the volume corresponding to those drop impressions having diameters within 0.00025 in. of the nominal or "mean" group diameter and the total volume for all such groups. It may be seen that for a given nozzle the average drop size decreases as the

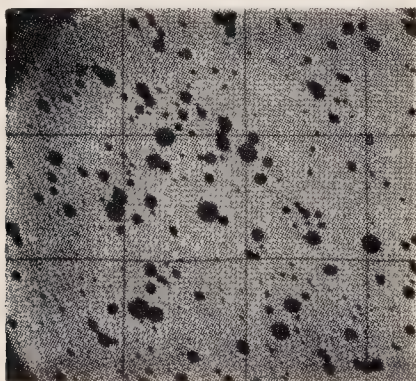


FIG. 3. Fuel drop impressions in lampblack surface.

injection pressure increases, although the change is not very great at the higher jet velocities. Other conclusions drawn from these tests were as follows: Decreasing the orifice diameter results in more uniform atomization of the spray and a smaller mean drop size. The density of the air into which the fuel is injected has little effect on the drop size distribution. Visual inspection of sprays cannot be used to estimate the relative drop size distribution.

Spark photographs⁶ of the symmetrical spray from a plain nozzle and of two views of the spray from a two-impinging-jets nozzle, each of which was injected into atmospheric air at a high jet velocity, are reproduced in Fig. 5. The multiple-orifice spray is simply a composite of plain

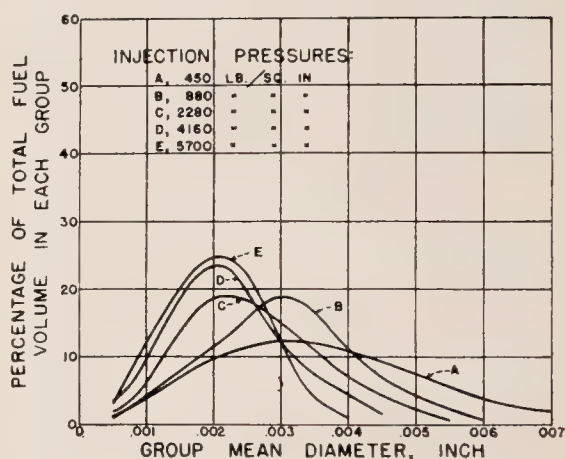


FIG. 4. Effect of jet velocity on atomization.

sprays, whereas the pintle nozzle gives a spray of greater lateral spread. At gas densities greater than atmospheric the spray penetration decreases, as is illustrated in Fig. 6 for two plain nozzles and an impinging-jets nozzle. The penetration into any gas is determined by the gas density rather than the gas pressure.⁴ For some applications the lower penetration of the impinging-jets nozzle may be advantageous, because of the greater lateral spread of the spray and the decreased impingement of the spray on the walls of the combustion chamber. Four such nozzles of the open type are used per cylinder in the Junkers aircraft Diesel. The length-diameter ratio of round-hole orifices giving the best spray penetration lies between 4 and 6, whereas the greatest lateral spread, or spray angle, occurs with ratios between 2 and 3.³ It is for this reason that the smaller orifices are shown countersunk in the multiple-orifice nozzle in Fig. 1.

Further information as to the relative spatial distribution of fuel in sprays from various nozzle types has been obtained⁷ by determining the

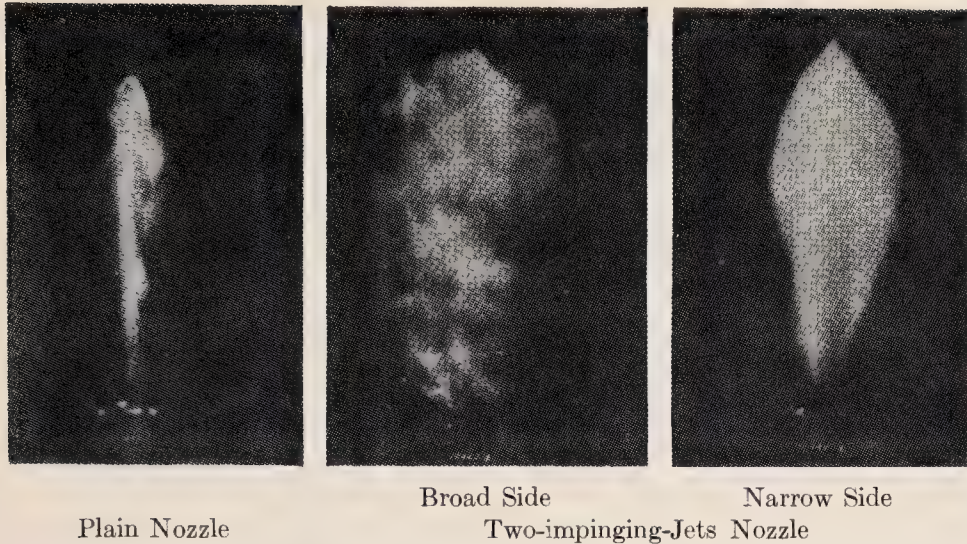


FIG. 5. Spark photographs of sprays injected into atmospheric air

quantity of fuel caught by suitable receiving apparatus set up in front of the nozzle for a definite number of injections into air of the desired density. Typical curves for the distribution obtained with three of the nozzle types shown in Fig. 1 are given in Fig. 7 for an air density fourteen times that of atmospheric air. The impinging-jets nozzle gave the best distribution within the spray, the pintle nozzle was intermediate, and the plain nozzle gave the poorest distribution. For plain round-hole orifice nozzles some improvement in lateral distribution within the spray resulted from an increase in injection pressure, the improvement being a function of orifice size. Low viscosity fuels also gave better distribution. The curves illustrate the difficulty of finding a satisfactory combination of orifice and combustion chamber design and the necessity of employing air movement within the combustion chamber to assist in the mixing of fuel and air. At present, the pintle

nozzle is widely used in commercial applications employing some form of precombustion chamber, but the multiorifice nozzle has been found most effective in tests at this laboratory with integral types of combustion chambers.

Combustion and Combustion Chamber Design

If it were not for the fact that available injection systems are incapable of distributing the fuel in a completely satisfactory manner, there would be little excuse for the varied combustion chamber designs that have been used in commercial Diesel engines. All such designs have as their basic purpose one or both of two aims: (1) to furnish supplementary fuel-air mixing to correct partially for the deficiency in the spray distribution and (2) to diminish the combustion shock or Diesel knock. As fuels of sufficiently high ignition quality are available, the problem of securing

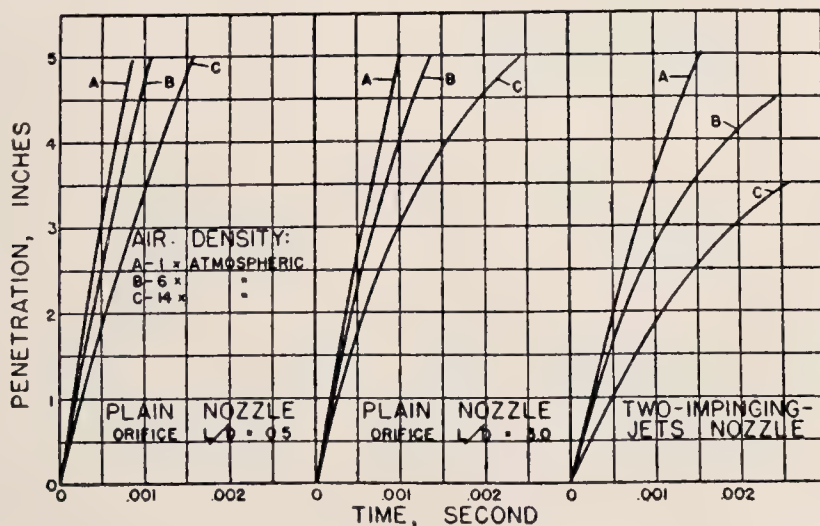


FIG. 6. Effect of air density on penetration of spray tip. Injection pressure = 4000 psi.

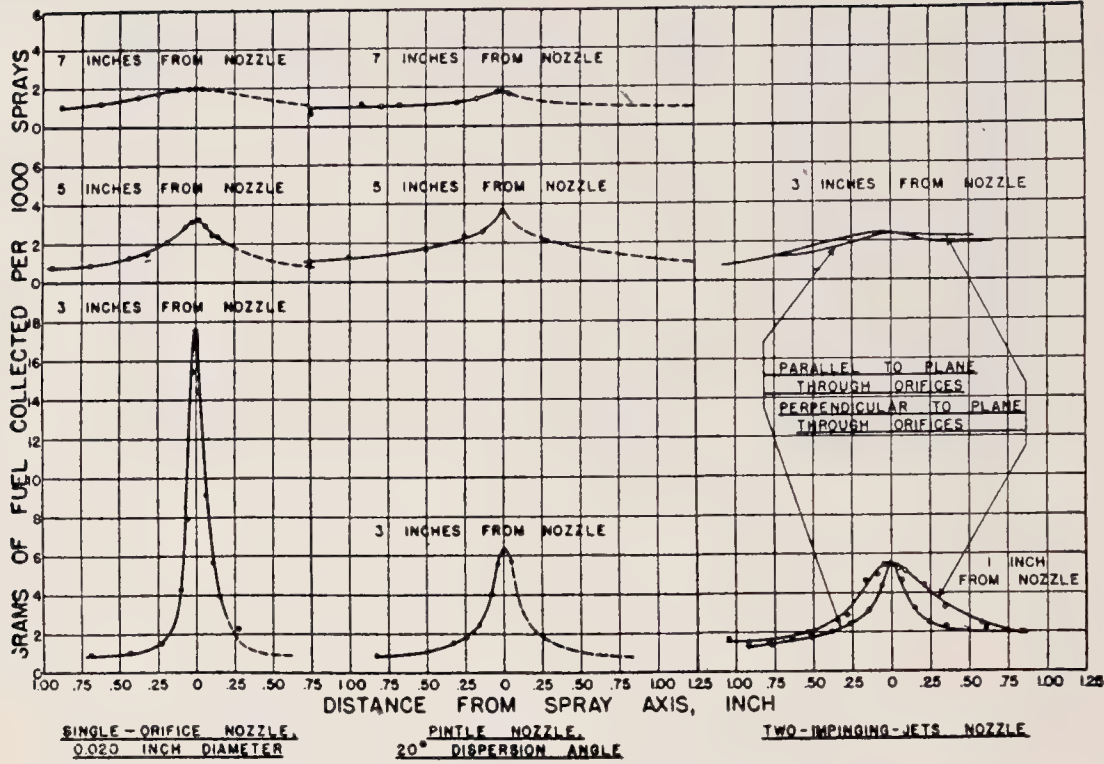


FIG. 7. Distribution of fuel within sprays.

adequate mixing is distinctly of greatest importance, particularly with high-speed engines. On this basis the combustion chamber should possess two characteristics: first, it should have a shape conducive to the best distribution of the fuel with respect to the air charge and second, it

should contribute as far as possible, by induced air flow and turbulence, to the secondary mixing of unburned or incompletely burned fuel with unused oxygen. Obviously an optimum coordination of injection system and combustion chamber shape minimizes the required auxiliary mixing by

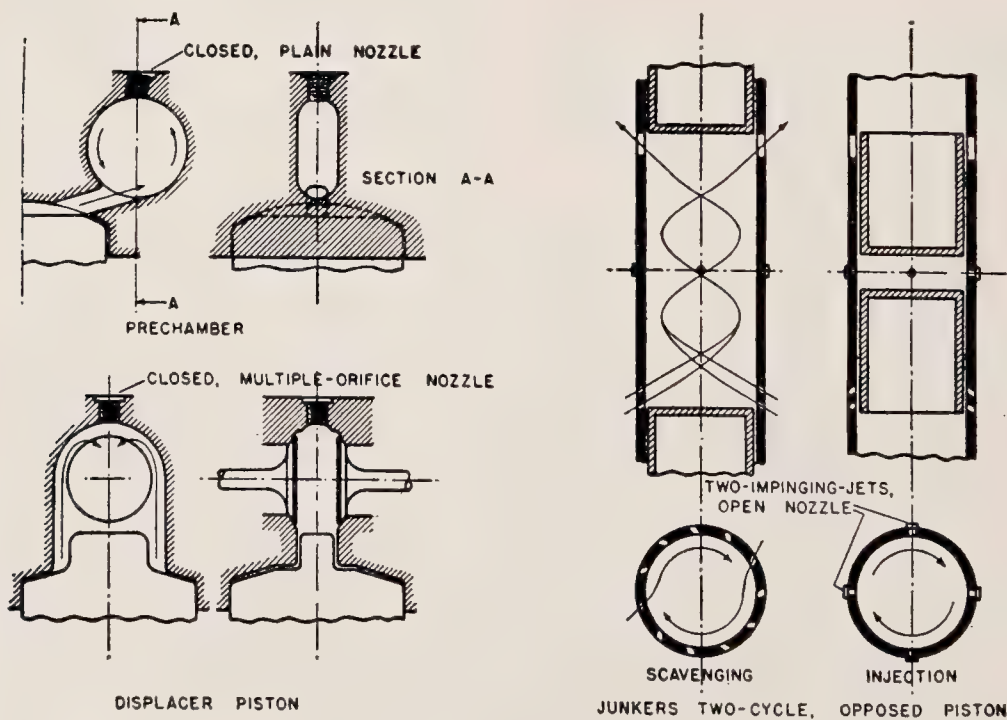


FIG. 8. Typical combustion chambers for inducing air flow.

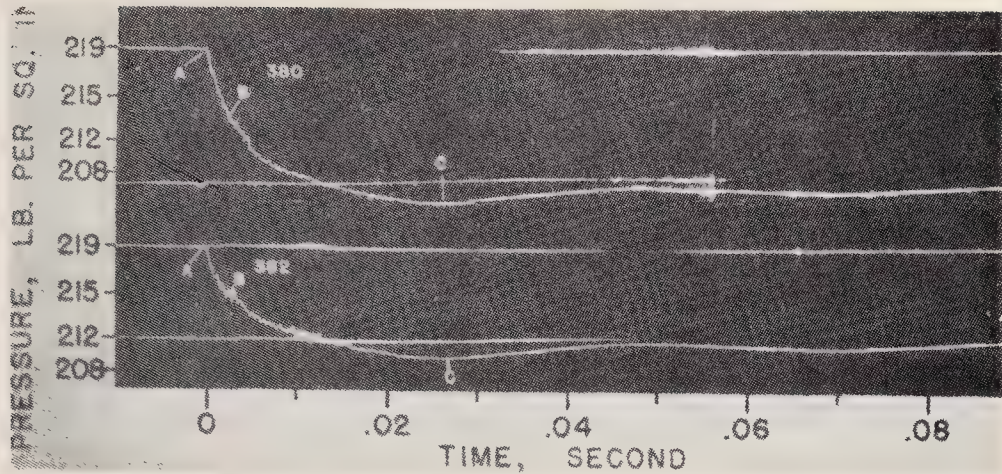


FIG. 9. Effect of fuel vapor concentration on rate of heat transfer.

air flow and turbulence. For this reason high dispersion or multiple-orifice nozzles generally give better results.

Three typical systems for obtaining air flow in the combustion space are illustrated diagrammatically in Fig. 8, each of these being at present an optimum design for its type. The air flow is induced by the restricted connecting passage between two portions of the combustion space in the prechamber type,⁹ and by the restriction between the combustion chamber and displacement volume during the latter part of the compression stroke in the displacer-piston type.^{10,11,13} In the Junkers two-cycle design the flow is generated by directed intake ports or baffles. It is particularly important to note that each design is basically a disk chamber in which is induced a directed flow of the air charge. The displacer-piston type is really an adaptation of

the so-called quiescent-chamber engine without any projection on the piston as developed by the National Advisory Committee for Aeronautics over a period of years.²

The fuel must not only be atomized and distributed throughout the air in the combustion chamber, but it must also be vaporized through absorption of heat from the air so as to form a combustible mixture. The rapidity with which the injected fuel absorbs heat from the surrounding air is indicated by Fig. 9.²³ The upper record shows the decrease in total gas pressure attending the heat transferred to Diesel fuel upon its injection into heated and compressed nitrogen. This decrease began with the very first portion of the fuel injected. The lower record corresponds to the third injection into the same air charge after reestablishment of thermal equilibrium following the first two injections.

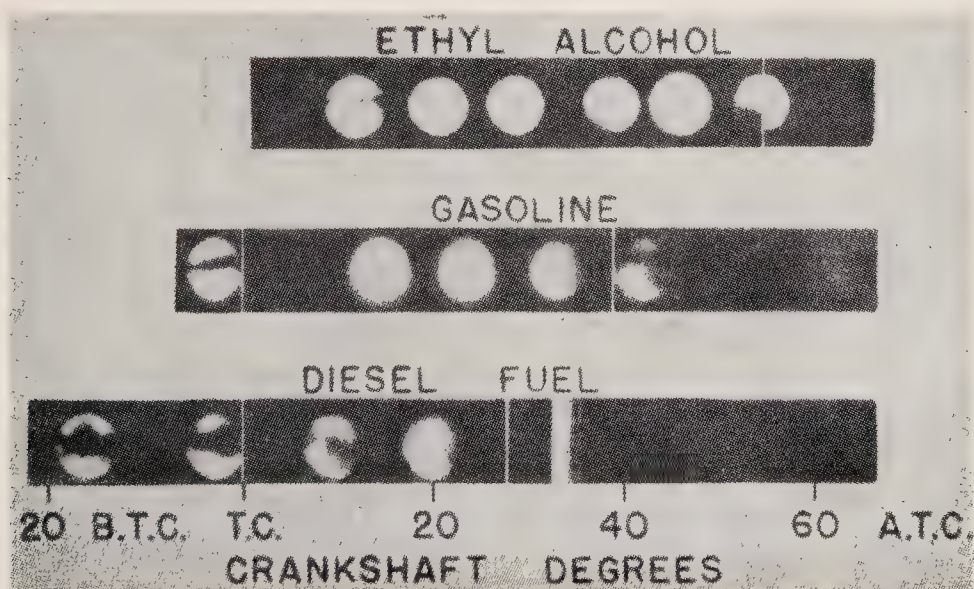


FIG. 10. Vaporization and condensation of fuel. Engine rpm = 1500; I.A.A. = 20°.

The decrease in the initial rate of pressure drop (or heat transfer) evident in the lower record must be attributed to one or both of the following: the greater heat capacity of the air-vapor mixture existing after the second injection, or an inhibition of the vaporization of a portion of the fuel, which presumably occurred in the absence of vapor.

An indication of the rapidity of the vaporization process in an engine is furnished by the high-speed motion pictures reproduced in Fig. 10.¹⁶ The photographs in each series were obtained by means of suitably timed sparks and show a silhouette of a quiescent combustion chamber provided with front and rear windows 2.5 in. in diameter. In taking the photographs, the engine was motored over and a single charge of fuel injected into the combustion chamber. Combustion was prevented by the extremely low temperature at which the engine was operating. Each series of photographs corresponds to a fuel having a dew point markedly different from that of the others, the injection advance angle being maintained constant. The chamber contents became more transparent as the spray core disappeared through its vaporization and its movement beyond the field of view. On the expansion stroke the contents of the chamber suddenly became opaque, as a result of the condensation of the vapors. The order of condensation in terms of crank angle was the same as that for the volatility or dew points of the fuels. The fact that the fuels were vaporizing was confirmed by the results of further tests in which the injection advance angle, the fuel quantity, the engine speed, and the engine temperature were varied independently.

The extent to which the fuel is mixed with the air in the combustion chamber can be studied by investigating the efficiency of the combustion and the efficiency with which the heat energy extracted from the fuel is transformed into useful work. By combustion efficiency is meant the fraction of available heat energy that is extracted from the fuel during the latter part of the compression stroke and during the power stroke. The efficiency with which this extracted heat energy is transformed into indicated work is termed the cycle efficiency. Although these two efficiencies are independent of each other, they are generally studied together. The product of these two efficiencies is the indicated thermal efficiency of the engine and is the factor of primary interest.

The extent to which the fuel is burned is indicated to a certain degree by high-speed motion pictures of the combustion process and to a greater degree by an analysis of the indicator cards taken during engine operation. High-speed

motion pictures were taken on the same single-cylinder quiescent-chamber test engine, operating under its own power for a single cycle, as was used for the vaporization work. In these tests the effects of high wall temperatures and of exhaust gas dilution were not present; otherwise, the test conditions meet very closely those experienced in actual engines. The quiescent chamber provided a minimum of air movement so that the distribution and dispersion of the fuel by the injection nozzle could be studied. Photographs of the injection and combustion of the fuel taken under this condition at a rate of about 2000 frames a second are presented in Fig. 11.¹⁹ The figure emphasizes the inadequacy of the fuel dispersion and distribution from a single round-hole orifice, and the improvement that is obtained from the multiorifice nozzle. With the single round-hole orifice the area reached by the flame indicates the area of the fuel dispersion. Although there is continual vaporizing of the fuel sprays, the spray core and at least part of the envelope are visible in every case up to the start of combustion. Much of the combustion chamber is never reached by the burning gases. With the six-orifice nozzle the flame not only reaches all the visible portion of the combustion chamber, but persists for an appreciable time interval. The fact that ignition often occurred between the sprays is of interest. The slit nozzle, although giving fairly uniform distribution throughout the spray, did not disperse the fuel throughout the chamber, so that the mixing was inferior to that given with the six-orifice nozzle, even though the latter contained the six dense spray cores. The dense core is apparently necessary to obtain sufficient spray penetration in a combustion chamber which does not have high-velocity air flow.

The effect of air flow on spray development and on combustion is shown in the three series of schlieren, high-speed, motion-picture photographs, together with the respective combustion chamber arrangements, as in Fig. 12.²⁰ Except for the definite deflection of the opaque fuel in the two lower series, these pictures do not convey the impression of air motion nearly so well as the projected motion pictures. Other than for the schlieren feature, the upper series of photographs is similar to that in Fig. 11. As the displacer on the piston, as shown opposite the second series, entered the combustion chamber a violent swirl of the air as a whole was produced in the chamber. Even though the spray core itself was not destroyed by the air swirl, a greater combustion chamber area was reached by the flame than was the case without the air movement. With the multiorifice nozzle and the two-passageway displacer the pictures indicate some air movement, but a

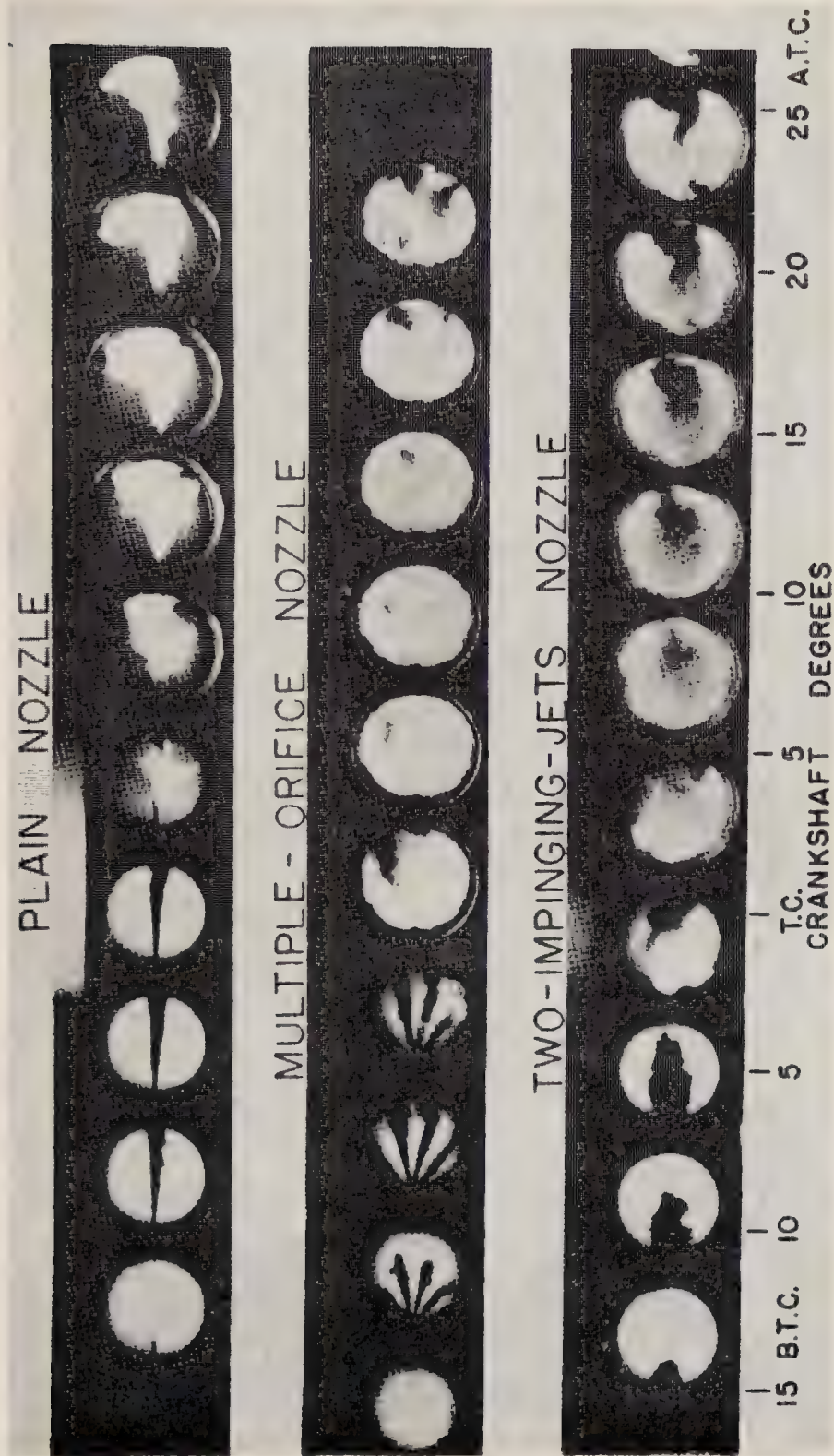


FIG. 11. Variation of fuel distribution and flame formation with nozzle design. Engine rpm = 1500; I.A.A. = 15°.



FIG. 12. Effect of air flow on fuel sprays. Engine rpm = 1500; I.A.A. = 15° to 20°.

comparison with similar pictures taken without air flow shows that there was no apparent improvement in the mixing of the fuel and air. Nevertheless, both the single and double passage displacers showed a decided improvement in performance for a combustion chamber of similar design on a single-cylinder test engine. Apparently with a nozzle that distributes the fuel reasonably well, the chief function of the air flow is not to disrupt completely the spray cores, but to improve the mixing between the individual sprays. In fact, it seems that the sprays contribute to the destruction of the air movement, but in so doing the desired mixing of the air and fuel is partially achieved.

By an adaptation of a method developed by Schweitzer²¹ for the analysis of engine indicator cards not only the combustion efficiency but also the cycle efficiency can be obtained to a fair degree of accuracy. The curves in Fig. 13 show the effect of fuel-injection advance angle (I.A.A.) on the indicator card and on the rate of combustion in the quiescent combustion chamber.¹⁴ The corresponding combustion and cycle efficiencies were computed from the indicator cards shown and the known fuel quantity injected. These efficiencies are given in Table I.

The data show that the ignition lag remained practically constant for the different conditions. Therefore it seems reasonable to believe that a factor equally important with the ignition lag is the time interval between spray cut-off and the start of rapid combustion. Spray photographic tests have shown that only after spray cut-off

TABLE I

Fuel-injection advance angle and efficiency

I.A.A.	Fuel-air ratio	Com-bustion efficiency	Cycle efficiency	Thermal efficiency
30	0.039	0.59	0.57	0.33
18	0.046	0.64	0.46	0.30
11	0.051	0.69	0.36	0.25

does the spray core disintegrate. A comparison of Fig. 13 and Table I shows that as the maximum rate of combustion was increased, the combustion efficiency also increased, but that the cycle efficiency decreased because of the lateness of the burning. As a result the thermal efficiency was highest for the earliest I.A.A. Had the tests been run on different fuels instead of different injection advance angles, then the fuel giving the highest combustion efficiency would also have given the highest thermal efficiency. This same effect has been obtained by using the same fuel and injection advance angle, but operating the engine at different jacket temperatures.² In these tests an increase in the jacket temperature decreased the ignition lag, but also decreased the combustion efficiency because of the shorter lag. These data have led to the conclusion that the Diesel engine should be operated on the lowest cetane number fuel consistent with easy starting and permissible rates of pressure rise.

Figure 13 also shows the long afterburning period that exists in most high-speed Diesel engines. Until means are derived for burning this fuel earlier in the expansion stroke, the cycle efficiencies inherent in the high expansion ratio of the Diesel engine will not be realized. In fact, the elimination of this afterburning period will probably do more to advance the Diesel engine than any other single factor. In other tests conducted by the National Advisory Committee for Aeronautics^{1,15,17} it has been shown that if the lag between cut-off of injection and start of combustion pressure rise is too great, the combustion efficiency and the combustion rates decrease. It appears, therefore, that there is a certain value of this lag which gives a maximum combustion efficiency and rate-of-pressure rise. For this reason, if the afterburning period can be eliminated, not only the cycle efficiency but perhaps the combustion efficiency as well will be increased.

The afterburning is probably caused by inadequate mixing of the fuel and air. This

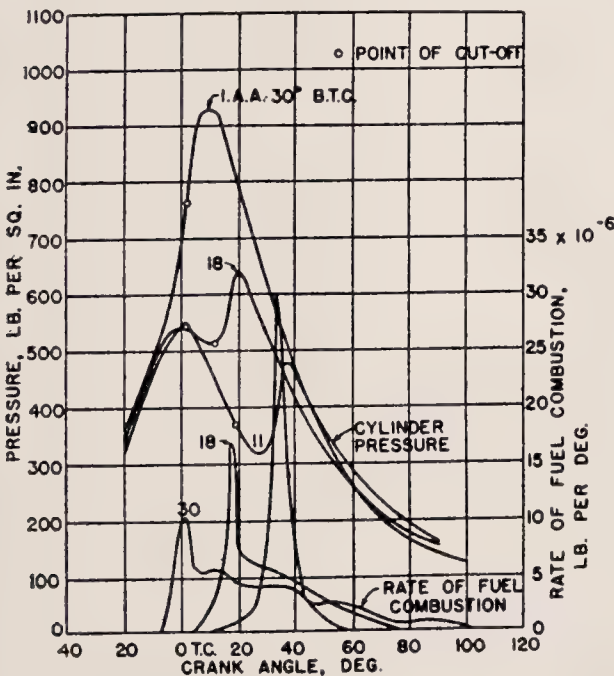


FIG. 13. Effect of injection advance angle on combustion rates.

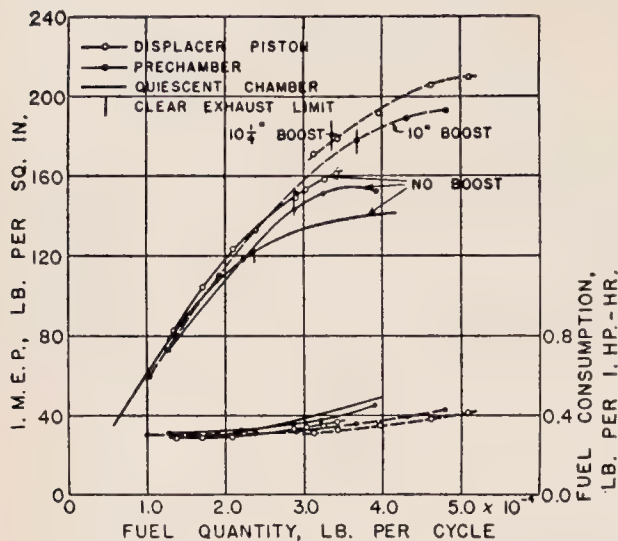


FIG. 14. Performance with typical combustion chambers.

mixing is controlled by the form of the fuel spray, the degree of atomization, the rate of fuel vaporization, the rate of vapor diffusion, and the degree and form of air movement within the combustion chamber. It is questionable whether any improvement in atomization over that obtained at present will further improve the distribution of the fuel. Tests were conducted at the laboratories of the National Advisory Committee for Aeronautics, in which a high-velocity air jet was directed through the injection nozzle with the fuel spray. Although atomization and burning tests showed the fuel to be much better atomized, the system did not give any improvement in engine performance. The rate of fuel vaporization is apparently comparatively high,¹⁶ and the test results indicate that, with the fuels used on commercial engines, the vaporization is sufficiently fast in every case to provide good mixing of the fuel and air. The diffusion of the fuel vapors appears to be too slow to provide adequate mixing even though nozzles with good distribution characteristics are employed.^{18,19} It can be concluded that the improvements in mixing must be obtained through close coordination of the spray form and the air flow in the combustion chamber.

It is evident from the solid curves in Fig. 14 that the indicated mean effective pressure and the specific fuel consumption improve with N.A.C.A. chamber design in the following order: quiescent chamber, prechamber, and quiescent chamber in combination with a displacer piston.^{2,9,11} The dashed curves show that the response to boosting (the boost data presented in this paper have not been corrected for super-charger power) measured in terms of the increase in indicated mean effective pressure is about the

same at 1500 rpm for the prechamber and displacer engines. The clear exhaust limit for the quiescent chamber occurs at a considerably lower fuel quantity than for the unboosted prechamber and displacer engines. Considered on the basis of the limiting indicated mean effective pressure with clear exhaust, the displacer piston possesses an advantage, either boosted or unboosted.

The displacer-piston tests have been extended to 2500 rpm and a boost of 20 in. of mercury, the resulting fuel consumption and maximum indicated mean effective pressure for a clear exhaust being 0.34 lb per indicated horsepower-hour and 235 psi, respectively, at a maximum cylinder pressure of 1200 psi.¹² These high performance figures at 2500 rpm result from a combination of one or more of the following factors: greater permissible maximum cylinder pressure, improved cylinder scavenging with inlet and exhaust valve overlap, and better response to boosting.

The improvement in thermal efficiency with boosting, as shown by the decrease in specific fuel consumption at the higher loads, is another notable feature shown by Fig. 14. This same tendency is again evident in Fig. 15.²² In this figure the ratio of the absolute explosion pressure 0.004 sec. after ignition to the initial pressure is plotted against the ignition lags obtained when the fuel charge is injected into a constant-volume bomb containing air at several respective temperatures and densities. The lower density approximates those existing in a Diesel engine at normal injection advance angles, whereas the higher density corresponds to that in an engine at top center operated with a boost of about 10 in. of mercury. The improvement in combustion efficiency with increasing density is appreciable,

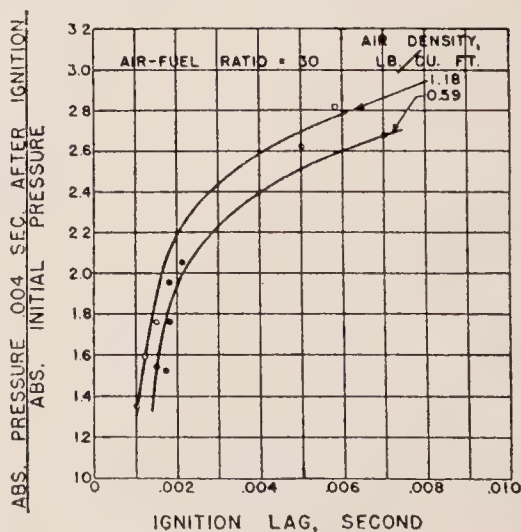


FIG. 15. Improvement in combustion with increasing air density.

particularly for the shorter ignition lags such as are permissible in engines.

Conclusion

From the data obtained on the high-speed Diesel engine at the laboratories of the National Advisory Committee for Aeronautics and at various other research institutions it is possible to draw certain definite conclusions and to outline the direction in which experimentation should go. One important conclusion is that the flat-disk combustion chamber offers the greatest promise. In the researches reported here, it was found that the flat-disk chamber gave the best performance with either the precombustion or the direct-injection chamber. In the precombustion chamber it was found that the best performance was obtained with most of the volume in the precombustion chamber of the flat-disk form. The outstanding performance obtained in Germany on the Junkers engine is also obtained with the flat-disk chamber. The chief difference between the three engines is in the nozzles used for the injection of fuel, the displacer-piston engine using a multiorifice nozzle, the precombustion chamber engine a single round-hole orifice nozzle, and the Junkers engine four impinging-jets nozzles. In each case the choice of nozzles has been the outcome of considerable experimentation and represents the best combination of combustion chamber design, air swirl, and nozzle design obtained so far. All three combustion chambers use a high-velocity air swirl, although the method of producing the swirl differs. The precombustion chamber engine has the disadvantage of an unscavenged space, which definitely limits its performance to a value below that of the other two types. More research is necessary on the effects of the design of the nozzle for the injection of fuel to determine, if possible, an optimum form of nozzle.

More data are necessary on the fuel distribution within the combustion chamber. There is little quantitative information on the distribution throughout the combustion chamber from the start of injection to the completion of the first 30 degrees of the expansion stroke. Finding the air-fuel ratio in different parts of the chamber during this time interval presents a difficult problem, but efforts to find it should be made. Tests should be conducted to determine whether the afterburning period is caused by inadequate mixing or by certain chemical phenomena. If it is chemical, it is possible that the use of certain fuel dopes will help to speed up the late burning.

Although it has not been brought out in this

paper, there is a need of data on the effect of the rate of injection on the combustion efficiency. It is probable that to obtain widely different rates with adequate nozzle distribution, it will be necessary to use a unit injector. The unit injector, in which the piston of the injection pump is mounted as closely as possible to the injection nozzle, shortens the comparatively long time interval for pressure changes to be transmitted throughout the injection system.

The question of fuel rating, which is proving so bothersome in the gasoline engine field, appears to be fairly straightforward for Diesel engines. There are at least two methods of Diesel fuel rating, either of which is satisfactory, namely, the ignition lag as measured in the engine or the ignition lag as measured in a bomb at temperatures and densities equivalent to those in the engine.

As the speed of the Diesel engine is increased there is going to be a need for even closer co-ordination of the injection system and combustion chamber design. In addition, the injection system will need further development in order to inject the fuel in the shortened permissible time. Here again, it is probable that the unit injector will be at an advantage over the systems in general use at present, in which there is an injection tube of appreciable length between the injection pump and the injection valve.

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METHODS OF RATING DIESEL FUELS

P. H. SCHWEITZER

School of Engineering, The Pennsylvania State College, State College, Pennsylvania

I. Mechanism of the Diesel Combustion Knock

The Diesel process is frequently described as injecting liquid fuel into highly heated air, the fuel igniting instantly upon its entrance into the cylinder. If this description were accurate, there would be no combustion knock in Diesel engines, generally speaking. The introduction of the fuel into the cylinder is a gradual process, if for no other than mechanical reasons. The injection extends over a period of 20 to 35 crank degrees, sometimes more, seldom less. During this period the introduction of the fuel is more or less uniform. If the ignition were instantaneous, the rate of pressure rise would follow the rate of injection and be moderate. Combustion knock, on the other hand, always is accompanied by a very rapid pressure rise.

However, the process described is upset by the ignition lag. The fuel injected does not ignite instantaneously. The significance of the delay period is discussed in another paper⁹ of this symposium. For us it will suffice to say that the longer the delay the more violent the subsequent ignition and the more severe the combustion knock.

Almost every factor that causes a spark-ignition engine to knock makes the compression-ignition engine run more smoothly.⁴⁵ In both cases the knock is caused by the autoignition of a considerable portion of the charge, but while in a spark-ignition engine it is ordinarily the last portion of the charge which autoignites, in the compression-ignition engine combustion is initiated by autoignition. This explains the different behavior of the two types of engines.

Consequently fuels of paraffinic base, consisting mostly of saturated straight-chain hydrocarbons, are the smoothest and most desirable fuels for Diesel engines, while cracked fuels and also straight-run aromatics burn roughly, benzene being about the worst of all. Gasoline antiknocks have the reverse effect in Diesels,⁴⁷ while pronknocks, consisting mostly of mild detonants like ethyl nitrate, added even in a small percentage reduce the Diesel knock remarkably. This is explained by the fact that paraffin fuels and ethyl nitrate ignite after a comparatively short delay and do not permit the accumulation of a considerable amount of combustible charge in the cylinder.

II. History of Diesel Fuel Testing

Rieppel,⁴³ in 1907, as one of the earliest research workers on the behavior of liquid fuels in compression-ignition engines, recognized that no relation existed between the flash point or burning point of a fuel and its ability to ignite spontaneously inside an engine cylinder.

Holm,²³ in 1913, investigated autoignition temperatures in oxygen by allowing oil globules to drop to a porcelain crucible cover heated inside a vertical tube furnace swept through by a stream of oxygen.

Constam and Schlaepfer¹³ continued the investigation with increased accuracy, but they could not share Holm's opinion that the spontaneous ignition temperature was of decisive influence on the suitability of fuel oils for Diesel engines.

A simple and successful autoignition temperature tester operating with air under atmospheric pressure was developed by Moore⁵⁶ in 1919, which has been perfected by Wollers and Ehmeke in the Krupp laboratories.⁵¹ In Jentsch's modification of the open crucible, the oxygen feed is closely controlled.

Compressed air in a bomb was used by Tausz and Schulte⁵⁰ and atomization of the fuel added by Hawkes¹⁶ Neumann,⁴⁹ Foord,¹⁵ Holfelder,²² and Michailovra.³³ These investigations have shown that self-ignition temperature depends to an enormous degree on the delay period and to an appreciable degree on the air pressure, density, air-fuel ratio, material of the crucible, and atomization of the fuel. By agitating the air in the bomb Neumann⁴⁹ obtained self-ignition temperatures that were much higher than those for stagnant air, except for very short ignition lags, when the reverse was true.

The above investigations rated Diesel fuels in somewhat similar order and have shown that paraffinic fuels have lower self-ignition temperatures than aromatic or naphthenic fuels. But the order of magnitude of the time lag in simple bomb tests was a multiple of 0.1 sec, compared to a few thousandths of a second obtained in compression-ignition engines. In recently constructed bombs, however, using high pressure, turbulence, and fuel atomization, ignition lags were measured³³ that are comparable with those obtained in engines.

In 1923, Hesselman¹⁸ described a method for measuring ignition lag, which he used on his

engine. In 1931, Le Mesurier and Stansfield²⁹ gave results of tests to determine the difference in behavior of a wide range of fuels in several compression-ignition engines, and showed that, in any given engine, the combustion knock was broadly related to the delay which occurred between the moment of injection and the beginning of rapid pressure rise, which they measured essentially in the same way as Hesselman. Different engines seemed to have only slightly different relative effects on the fuels tested.

In the same year Boerlage and Broeze⁶ published their results on an engine-test method of rating Diesel fuels. The tests were made in a relatively slow speed engine by the throttling method, and each fuel was rated in terms of the blend of cetene and mesitylene which matched it in ignition lag. The tests have shown surprisingly good correlations, indicating not only that the method is dependable but also that differences between engines and running conditions were of relatively slight effect upon the rating.

In January 1932, Pope and Murdock⁴⁰ reported on their tests made with a modified C.F.R. knock-testing engine. In these tests the engine was of the variable compression type, and the rating was based on the lowest compression ratio at which the samples of fuel would just ignite under controlled temperature conditions. While running the engine under such borderline conditions did not prove practical, with a "motored engine" the critical compression ratio method gave very useful results.

In July 1932, Boerlage and Broeze⁷ proposed that ratings in ignition quality be made in terms of "cetene numbers", using cetene and alpha-methylnaphthalene as primary standard. In 1935 the A.S.T.M.¹ replaced cetene in this country by cetane for a standard reference fuel of high ignition quality.

Until recently, ignition lag determinations were made from indicator diagrams. In 1932, Boerlage and Broeze⁷ described an inertia lag meter, and a year later⁸ reported cetene ratings performed with a modified Midgley type bouncing pin. The "knockmeter delay method" which has been most widely used in this country is an outgrowth of this method, and was developed by Rendel⁴¹ in cooperation with the Waukesha Motor Company, the builders of the converted C.F.R. engine which has been tentatively adopted for Diesel fuel rating.

In 1933, Schweitzer, Dickinson, and Reed⁴⁶ proposed the use of a predetermined ignition lag, to be obtained by a corresponding adjustment of the compression ratio, for rating. In 1935, Hetzel and Schweitzer²⁰ replaced the bouncing pin by a magnetic pick-up, which flashed the neon lamp of a protractor through an electronic relay.

One of the first empirical equations based on physicochemical data, and indicative of the ignition quality of the fuel, was proposed in 1931 by Butler¹¹ and called "Ignition index":

Ignition index

$$= (1 - \text{specific gravity}) \frac{\text{specific gravity}}{\text{dispersion}} \\ \times \text{average boiling point (}^{\circ}\text{F)}$$

The specific gravity and dispersion are to be taken at 100°F. This was superseded in 1934 by the Diesel index of Becker and Fisher⁴—a formula involving gravity and aniline point which has subsequently become rather popular.

In the same year, Moore and Kaye³⁵ proposed the viscosity-gravity number, which has been modified by Hill and Coates²¹; this formula contains only viscosity and gravity.

One year later, Jackson²⁶ proposed the boiling point-gravity number, which uses the 50 per cent distillation point and gravity in a formula.

In 1935, Heinze¹⁷ proposed as an index the parachor of Sugden,⁴⁹ $p = S^{\frac{1}{2}}/D$, where S = surface tension and D = specific gravity. When p is plotted against the molecular weight, characteristic straight lines are obtained, one for each class of hydrocarbons, which correlates well with the cetane rating.

The U.O.P. (Universal Oil Products) characterization factor, proposed by Hubner and Murphy²⁵ in 1935, includes the same factors as the boiling point-gravity number in a different combination.

As a further refinement, in 1937, Hubner²⁴ introduced the ignition quality number, which is obtained by multiplying the Diesel index by the 50 per cent distillation point.

Marder and Schneider's formula³² based on the boiling point index and Kreulen's "ring analysis"²⁸ are the most recent contributions along this line.

III. Scale for Expressing Rating

No matter what testing method is adopted for measuring ignition quality, it is essential to determine the manner in which the rating of the fuel shall be expressed. This problem is only loosely related to the method of rating. Using the engine rating, one way to express the rating would be to use the measured factor for scale, as the ignition lag in degrees, the lowest usable compression ratio, the required compression ratio to produce a predetermined ignition lag, the maximum rate of pressure rise, and others.

Another way to express the rating is based on two standard reference fuels, one of high and the other of low ignition quality. The test fuel is

matched with a blend of the two reference fuels mixed in such proportion that its ignition quality (in the arbitrary scale of the test) is equal to that of the reference blend. The rating of the fuel is then expressed as the percentage concentration of the reference fuel of high quality.

This second method can be used with any testing method that may be adopted—bomb, physicochemical, or engine tests—and it offers certain distinct advantages. Rating expressed in a reference fuel scale is no doubt less affected by the instrument factors. But the deciding consideration in the adoption of the cetene (later cetane) scale was the preceding experience with gasoline knock rating. In the early period that was expressed by Ricardo's H.U.C.R. (highest useful compression ratio), but that gave way first to the toluene equivalent and later to the octane number. Technologists accustomed to the octane number were quick to adopt the cetene number when it was proposed by Boerlage and Broeze.

The selection of the reference fuels required, however, a careful study. For reproducibility they should be pure substances of a known chemical composition, which are stable in storage. For range they should possess higher and lower ignition quality, respectively, than any fuel to be tested. For validity they should possess a chemical constitution and physical properties (viscosity and volatility) not much different from those of the normal fuels. Finally, they should be available at a reasonable price.

TABLE I

Properties of cetane and alpha-methylnaphthalene

Properties	Cetane*	Alpha-methylnaphthalene†
Specific gravity 60/60 °F	0.778	1.018
Flash point, closed cup, °F	230+	214
Pour point, °F	+65	+50
Viscosity, SSU at 100 °F	38	37
Distillation range, °F:		
Initial boiling point	516	450
10 per cent	532	456
50 per cent	534	438
90 per cent	536	460
End point	543	482
Aniline point, °F	204.0	Miscible

* As supplied by E. I. du Pont de Nemours and Company.

† As supplied by Reilly Tar and Chemical Company.

The reference fuels which were adopted by the A.S.T.M. as most satisfying these requirements are cetane, $C_{16}H_{34}$, and alpha-methylnaphthalene, $C_{11}H_{10}$. The properties of these substances are given in Table I.

Table I shows that the properties of these hydrocarbons are in line with those petroleum fuels which are used most in high-speed compression-ignition engines. The ignition quality of cetane is about equal to that of cetene, $C_{16}H_{32}$, but it is claimed that it is more stable in storage.

Since June, 1935, when the A.S.T.M. recommended its use, the cetane scale has become practically universal in this country as a measure of ignition quality. In Europe the use of the cetene number scale has been continued to date.

IV. Three Groups of Test Methods

A. Bomb Tests

The primary objective with the crucible and bomb tests was to determine the self-ignition temperature of the fuel. It has been observed that fuels of high self-ignition temperature either fail to ignite at all in the engine, or if they do ignite there is a long delay with a corresponding combustion knock. So self-ignition temperature was taken for a measure of ignition quality. The Moore apparatus uses an open porcelain crucible heated in a furnace or solder bath into which drops of oil are admitted while the temperature of the crucible is raised by small increments until the fuel autoignites. This method was simple and well adapted to laboratory practice. It was found,^{4-6,29} however, that the self-ignition temperatures obtained with such an apparatus lie too close together and, furthermore, they do not rate fuels in the same order as their engine behavior. This should not surprise us, if we realize that temperature is just one of the many factors that determine autoignition. Others are chamber pressure, air motion, fuel drop size, fuel-air ratio, and time lag of ignition. Bridgeman and Marvin¹⁰ have shown that even the size and material of the crucible influenced the self-ignition temperature.

Subsequent efforts have been directed at creating conditions in an ignition bomb similar to those in the engine, and improved ignition testers have been evolved. Such recent variants as Holfelder's²² and Michailovra's³³ inject finely atomized sprays into heated dense air, agitated to simulate turbulence, and measure the delay of the ignition. The results obtained are comparable to and correlate well with engine tests. By the time the bomb has reached this perfection it has become so complicated that it now offers no

advantage either in first cost or in ease of operation over the test engine.

The ideal that self-ignition temperature as a characteristic property of the fuel would determine its ignition behavior did not materialize. Whether or not a fuel drop ignites at a certain temperature depends a great deal on how long the drop is exposed to that temperature and, furthermore, the time sensitivities of the various fuels are different. The determination of the maximum or minimum ignition temperatures, which correspond to zero or infinite time lags, respectively, is of theoretical interest, but the existence of neither of them has yet been proved.

B. Engine Tests

The success of the gasoline knock-testing engine encouraged the search for a method that looks for an answer on Diesel fuel quality in the engine itself. The possibility of using the gasoline knock-testing engine unaltered suggested itself. From the reverse behavior of the fuel in spark-ignition and compression-ignition engines it was not unreasonable to expect that Diesel fuels would rank in the reverse order as their octane numbers or directly as their "heptane numbers". One practical drawback to this method has been the difficulty of carbureting heavy oils and the trouble these oils cause in the engine by gumming, coking, crankcase dilution, etc. Dumanois¹⁴ overcame these difficulties by mixing 15 per cent Diesel fuel with reference gasoline. The knock

rating of such mixtures in the gasoline knock-testing engine was found to correlate fairly well with the behavior of the heavy oil in the Diesel engine. But at the same time the tests have shown²⁵ that it is too much to hope for a perfect reciprocity in a spark-ignition and compression-ignition engine that would justify the universal adoption of the gasoline-testing method for Diesel fuels. If a larger margin of error is admissible this simple method of rating Diesel fuels is recommended.

There is no apparatus that simulates the compression-ignition engine conditions as much as a compression-ignition engine itself. The use of a compression-ignition engine for testing the ignition quality of fuels started in 1931 and attained considerable momentum recently. A variety of methods have been used by Le Mesurier and Stansfield,²⁹ Boerlage and Broeze,⁶ Pope and Murdock,⁴⁰ Joachim,²⁷ Rendel,⁴¹ and Schweitzer and Hetzel.⁴⁷ In principle, however, all of these agreed. The ignition quality as such is not measured by any engine test, but is only determined indirectly on the basis of the behavior of the fuel in the test engine in regard to such characteristics as combustion knock, ignition lag, rate of pressure rise, starting, or misfiring.

A valid objection to engine test methods is that the results they give have no *theoretical* significance, and cannot be expressed in terms of ordinary physical units. However, in view of the great *practical* significance of fuel rating, this

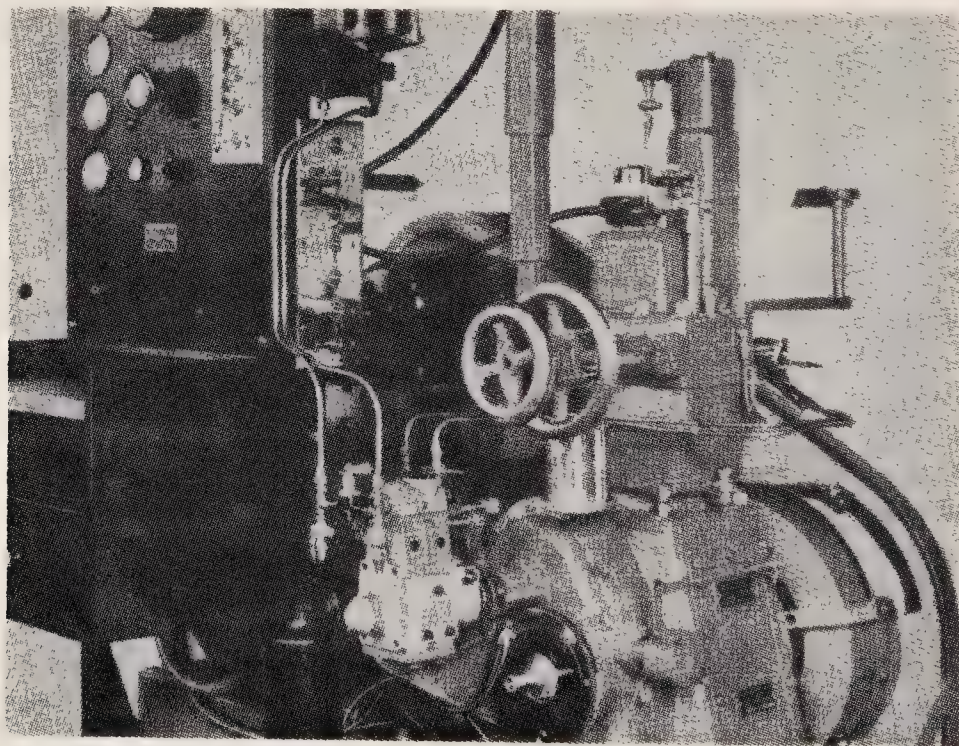


FIG. 1. C.F.R. engine for Diesel fuel testing developed by the Waukesha Motor Company

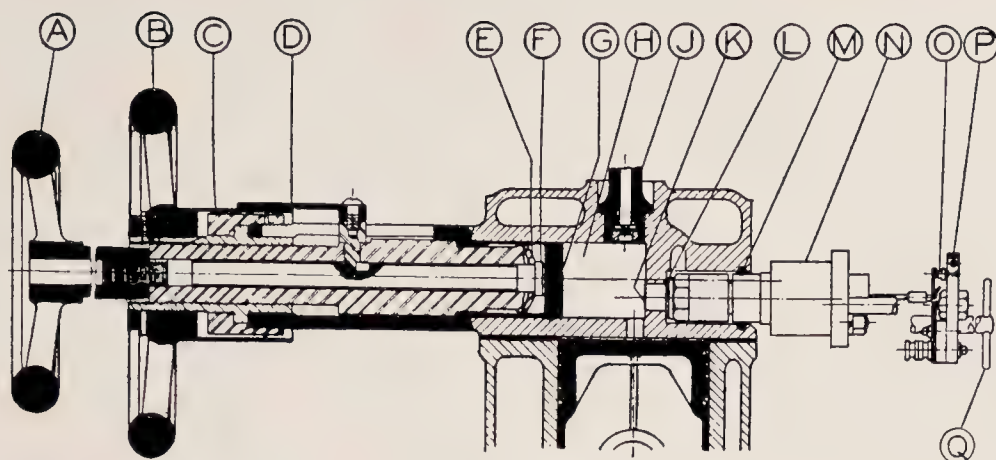


FIG. 2. Diesel variable compression plug. Optical delay method. Cross section of cylinder head showing mechanism for varying volume of combustion chamber.

objection can be set aside as it was set aside in the case of knock rating of gasolines.

Another objection that has been raised against this type of testing is that its practical significance is limited to the type of engine with which the tests have been performed. Doubts regarding the general nature and applicability of the ratings obtained by engine tests have been largely dispersed by investigations performed on a great number of engines by Boerlage and Broeze,⁶ Stansfield,⁴⁸ Joachim,²⁷ MacGregor, and Good.⁵¹ The results have shown⁴⁶ that (1) with few exceptions, for which the reasons are clear, all engines rate fuels in substantially the same order; (2) the results obtained in any engine are not unduly sensitive to the engine factors such as amount of fuel, type of spray, injection timing, etc. These statements are rather general and do not apply equally to all types of engine that have been proposed, but accumulated evidence tends to indicate that the behavior of Diesel engines with regard to cetane rating is much more uniform than the behavior of spark-ignition engines with regard to octane rating.

1. *Test Engine.* Broadly speaking, any engine is suitable for fuel testing. This fact was recognized by the Institute of Petroleum Technologists^{25a} by permitting the use of any engine for the determination of fuel ignition quality. In this country the converted C.F.R. engine, built by the Waukesha Motor Company, has been used almost universally for fuel testing. The engine is shown in Fig. 1 and the cross section of the head in Fig. 2. It is a $3\frac{1}{2} \times 4\frac{1}{4}$ ", one-cylinder, four-cycle engine with a swirl-type combustion chamber provided with an adjustment plug which permits changing the compression ratio between 6:1 and 28:1. An induction type generator supplies the load and maintains the

speed constant. Otherwise, the engine is conventional except that it is provided with heaters for the intake air, cooling water, and lubricating oil which permit keeping these at a predetermined value.

The chief advantage of the Waukesha type of test engine is its variable compression ratio. An engine with a fixed compression ratio can only test fuels of a limited range, while the variable compression ratio not only enables the engine to burn a wide range of fuels but by suitable adjustment the engine can be made sensitive to the ignition quality of the test fuel.

2. *On the Selection of a Suitable Ignition Index.* In testing the ignition quality of fuels in an engine the fuels are compared on the basis of some suitable index such as knock, pressure, ignition lag, etc. The engine as a testing instrument cannot be expected to measure the ignition quality of a fuel in physical units. But a rating can be based on engine tests if the engine is able to indicate that one fuel has a higher ignition quality than another. With the use of the cetane scale the engine test is boiled down to answering the simple question: Are the ignition qualities of two given fuels equal? If not, which is higher?

Several criteria can be used for answering this question. Those that have received wider attention are (1) combustion knock, (2) pressure rise, (3) rate of pressure rise, (4) ignition lag, (5) misfire, and (6) computed combustion knock. These will be discussed briefly:

(1) *Combustion knock* is a factor with which the user is directly concerned. It can be judged from a casual inspection of the running engine. The aural observation, however, is too inaccurate to serve as a basis for test. Le Mesurier and Stansfield²⁹ compared fourteen Diesel fuels on the basis of audibility of combustion knock estimated by

ear. In the Junkers engine, which had an integral combustion chamber, the comparative rating of the fuels was the same at any speed between 300 and 1000 rpm. On the other hand, in the McLaren-Benz engine, which is of the precombustion chamber type, the order of merit changed with the speed.

Another difficulty with audibility tests is that it is not always easy to discriminate between combustion knock and other engine noises. To eliminate the latter difficulty and also the personal element in sound estimation, Carpenter and Stansfield¹² developed the strobophonometer, which measures the noise of a certain phase of the cycle by means of a mechanically driven selector and a suitable microphone. The noise readings obtained with this instrument correlated fairly well with ignition lag measurements and rate of pressure rise measurements.

(2) *Pressure rise* is frequently used as a measure of engine roughness. The maximum explosion pressure cannot be used as a measure of roughness,⁶ because an increase in intake air pressure increases the maximum pressure but at the same time makes the engine run more smoothly. It was also observed that the effect of fuel on the maximum pressure is indefinite. Good, bad, and indifferent fuels sometimes happen to have about the same combustion pressure rise. For these reasons pressure has never been considered as a suitable index of ignition quality.

(3) *Rate of pressure rise* is defined as the derivative of the pressure on the basis of time or crank angle. It is an indirect measure of the rapidity of burning. It was observed that combustion knock is always accompanied by a rapid rate of pressure rise. The correlation between shock audibility and maximum rate of pressure rise was found to be about 90 per cent.^{29,45} The correlation between ignition lag and maximum rate of pressure rise was equally high.

In early investigations maximum rate of pressure rise was determined by drawing tangents to crank angle base indicator cards. The observation was made that if the M.R.P.R. (maximum rate of pressure rise) is less than 30 psi per degree of crank motion, the operation is smooth. The engine is liable to knock if the M.R.P.R. is above 50 lb. per degree and is almost certain to knock if the rise exceeds 100 lb. per degree crank angle.

At present instruments are available which give the maximum rate of pressure rise directly, instead of deriving it from a pressure curve. By using an electromagnetic pick-up in connection with a diaphragm in the cylinder head, the flexing of the diaphragm which follows the pressure generates voltage in proportion to the

flexing (flux-cutting) velocity. This voltage can be impressed on a cathode ray oscillograph and the M.R.P.R. scaled as the maximum deflection of the light point on the screen.

The Sunbury knock indicator,³ which has been introduced recently for knock rating gasolines, is using this principle. Here, the magnified output of the magnetic pick-up is fed into a damped millivoltmeter and the reading is a measure of the average rate of pressure rise. The use of this instrument for Diesel fuel testing deserves serious consideration.

(4) *Ignition lag* is the time interval between the point of injection and the point of ignition. It has been used as the preferred index of ignition quality since the investigations of Le Mesurier and Stansfield²⁹ and of Boerlage and Broeze⁶ have established the close relations that exist between ignition lag and fuel quality as evidenced by combustion knock and difficulty of starting. The shorter the ignition lag of the fuel, the more quietly the engine runs and the more easily it starts if other conditions are the same. The principle of most current methods of measuring ignition quality is to match the sample fuel with a reference fuel which has the same ignition lag in a standard test engine under standard operating conditions or in the user's engine under the user's normal operating conditions.

The ease with which the ignition lag can be measured was no doubt a factor in its adoption for testing. In spring-loaded nozzles the beginning of the injection coincides with the beginning of the valve lift and can be determined very accurately by electrical means if the valve stem is accessible, as it usually is. The ignition point, on the other hand, was obtained from the indicator card, which regularly shows a readily noticeable pressure rise where ignition sets in.

While in most cases the determination of the

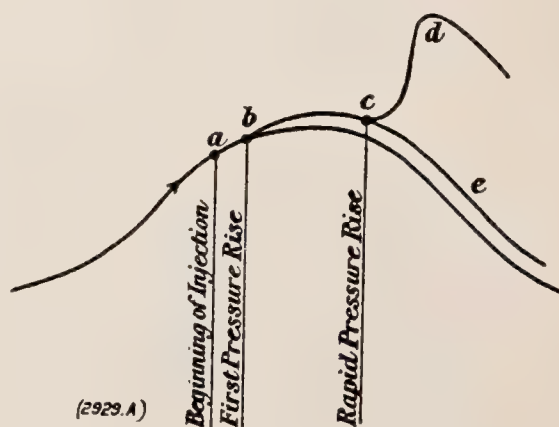


FIG. 3. Definition of point of ignition
(Boerlage and Broeze)

ignition point from the indicator diagram offers no difficulty, in cases like that shown in Fig. 3, a more exact definition is needed. Ignition point is frequently defined as the point where the pressure rises above the compression pressure (Point b, Fig. 3). Boerlage and Broeze⁶ are of the opinion, however, that the ignition point so defined is not significant of the knock or of the ignition quality of the fuel. They advocate the use of the first *appreciable* pressure rise (Point c, Fig. 3) as ignition point. Hetzel¹⁹ has, in fact, shown by oscillograms that by successively decreasing the compression ratio the point of appreciable pressure rise occurred later and later while the point of *initial* pressure rise was the same. Ignition point has also been variously defined as the time of first flame formation as detected by the human eye on a photographic film²² or by a photocell,⁴⁴ but for routine testing this is probably still less significant, as incandescence is of no immediate concern.

For the purpose on hand the definition of Boerlage and Broeze seems the most appropriate, although it is realized that in certain cases it must be arbitrarily decided when the rate becomes "appreciable."

(5) *Misfire* occurs if the compression ratio is not high enough to cause ignition. Since fuels of low ignition quality misfire at higher compression ratios than fuels of high ignition quality, misfire can and is being used as an index of ignition quality. In using the cetane scale the procedure again consists of matching the sample fuel with a reference fuel which misfires under identical conditions. A misfiring condition may be brought about by various methods. In a running engine one may reduce the compression ratio (if it is a variable compression engine), or decrease the intake air pressure (by throttling), or retard the injection timing, or decrease the jacket water temperature to the point at which misfiring occurs. The other alternative is motoring the

engine with injection shut off until it reaches stable temperature. Then the ignition is turned on. If no ignition takes place the compression ratio (or the other factors) is raised until ignition does take place. The borderline of misfiring is thus determined.

Two methods involving misfiring have become popular for fuel testing. The C.C.R. (critical compression ratio) method⁴⁰ is using a motored engine, and the test is sometimes referred to as the starting test, as it simulates starting conditions. The throttling method throttles the intake air of a running engine until the engine misfires. This method sometimes is referred to as the altitude test. Both of these misfiring tests give a high correlation with the ratings obtained by the delay methods.

(6) *Computed combustion knock* has been introduced by Joachim²⁷ and is defined as the product of the "explosion pressure rise" and the rate of pressure rise which takes place during the "initial burning period" (see Fig. 4). Its numerical value is obtained by the formula

Computed knock

$$= \frac{(\text{explosion pressure rise})^2}{\text{initial burning period} \times 10^4}$$

where explosion pressure rise is expressed in psi and initial burning period in degrees crank angle. The formula has merit, and remarkably good correlation has been shown³¹ between it and ratings obtained with conventional methods. Its chief disadvantage is that the "initial burning period" is seldom sharply defined and is frequently difficult to determine.³⁴

3. *Three Requirements of a Good Testing Method.* Any satisfactory testing method has to satisfy three requirements: (1) convenience, (2) reproducibility, and (3) validity.

For convenience a testing method is preferred

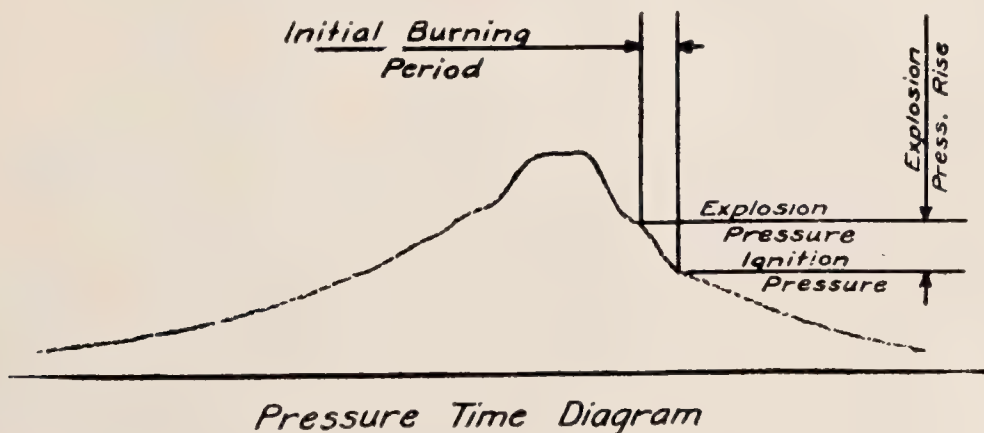


FIG. 4. Definition of compound combustion knock (Joachim).

which is quick and simple, and does not require elaborate instrumentation and numerous delicate adjustments.

It is only a truism that a good testing method *should* give reproducible results. It is no less a truism that a properly standardized test cannot but give reproducible results. The essence of the matter, however, is that it is not desirable or even possible to standardize a great number of factors to an absolute accuracy, with no tolerance permitted. If slight variations in some factors cause a great variation in the test result, the reproducibility is poor. The same term is applied if the test result is affected by factors the control of which is difficult or impossible. The term "reproducibility" is used in this sense in this discussion.

"Validity" means that the results of the test are representative and give exactly the information the observer is seeking. If the observer is interested in the wear resistance of a metal, the Brinell hardness test is valid, but a test of tensile strength is not. It is not easy to determine the validity of a test on ignition quality, because we have no exact definition of what ignition quality is. It is generally understood that Diesel fuels of high ignition quality start more easily, run more smoothly, and begin to misfire later than fuels of low ignition quality. But there is no conclusive evidence that these three things mean one and the same thing and, for that matter, we do not even know what any one of them means. The fact that has been established by numerous investigations is this: If by any arbitrary tests a group of fuels is ranged in the order of their resistance to misfire, then in the order of their ease of starting, then in the order of their smoothness of running, the three orders will be not exactly, but substantially, the same. It also has been shown that engines of various types and sizes rate the fuel in substantially the same order. These observations form the justification of the ignition quality testing. But not every test shows equally good correlation. The validity of a testing method will be considered high if its correlation is high with other tests and tests on other engines. The behavior of the fuels in service engines is considered most significant from the standpoint of validity.

To judge the various fuel-testing methods that have been proposed they are to be examined as to the extent to which they satisfy the three basic requirements of convenience, reproducibility, and validity. Some of these can be decided even without considering the details of the particular testing technique.

Tests based on the audible knock have not been used to any extent in routine testing because

they are inconvenient. No simple measuring instrument is available for the purpose.

Tests using the maximum pressure or combustion pressure rise for index of ignition quality must be ruled out on the lack of validity.

Maximum rate of pressure rise, on the other hand, correlates fairly well with valid indices, and the test can be made conveniently with simple instruments. While this type of test has not yet been proposed formally we have given considerable attention to it. As a result, the author's opinion is that the weakness of the M.R.P.R. test is its poor reproducibility.

For perfect reproducibility the engine and operating conditions have to be standardized with any testing method. But a desirable ignition index is one that is most sensitive to fuel quality and least sensitive to engine factors, particularly to those that are difficult to control.

The more important engine factors are as follows: engine speed, jacket temperature, inlet air temperature and pressure, compression ratio, combustion chamber shape, injection timing, injected fuel quantity (load), and nozzle opening pressure. Of these, injection timing seems to give the most trouble.

On many engines the injection timing can be controlled and read, on some it can be controlled but not read, and on some others it can be neither controlled nor read. Test engines as a rule permit setting the injection point at will, but an error of up to 0.5° can be committed easily. When changing from one fuel to another of different viscosity or gravity, the injection advance angle changes with unchanged injection setting. For these reasons an index of ignition quality which

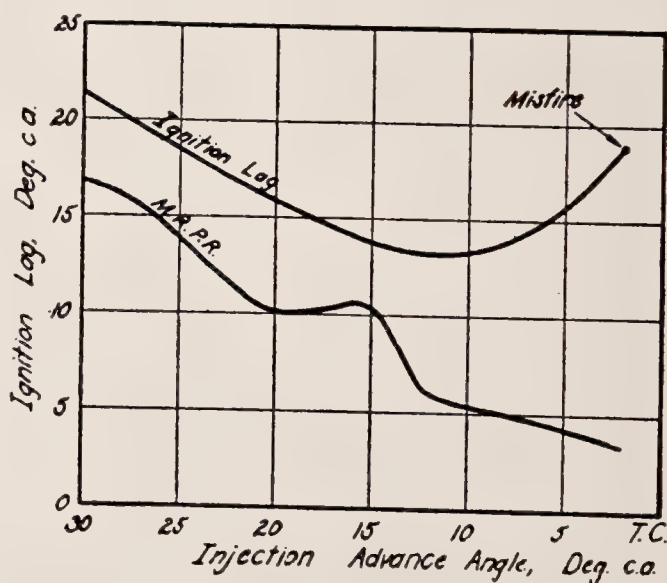


FIG. 5. Effect of injection timing on ignition lag and maximum rate or pressure rise (arbitrary scale).

is not unduly sensitive to injection timing is clearly preferred.

4. *Effect of Injection Timing.* Injection timing in an engine is controlled ordinarily by the fuel injection pump, but the beginning of pump delivery should not be taken as the beginning of the injection. The actual injection, corresponding to the exit of the first drop of fuel from the spray nozzle, always takes place later, the injection lag varying with the injection tube length, engine speed, fuel viscosity, injection quantity, etc. Therefore a fixed pump injection does not mean a constant injection timing. The injection point may vary 5 degrees crank angle or more according to engine speed, fuel viscosity, injection quantity, etc.

The effect of the injection advance angle on the maximum rate of pressure rise is erratic. Figure 5 is an example, where the wavy line shows the maximum rate of pressure rise in an arbitrary scale and the heavy line the ignition lag in degrees crank angle. When the injection is advanced from top center to 12 degrees before top center the M.R.P.R. rises, because the combustion approaches constant volume conditions. But at the same time the ignition delay period is also advanced, coming closer and closer to the high temperature zone near top center and becoming shorter and shorter. The shorter ignition lag reduces the amount of vaporized fuel accumulated at the moment of ignition and tends to reduce the

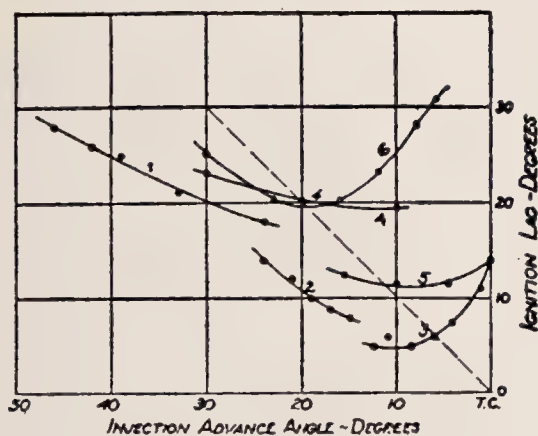


FIG. 6. Effect of injection timing on ignition lag in various types of engines. Curve 1, open combustion chamber, slight air swirl (Dicksee); curve 2, divided combustion chamber, moderate air flow (Dicksee); curve 3, divided combustion chamber, vigorous air flow (Dicksee); curve 4, open combustion chamber, negligible air flow, Bosch pump (N.A.C.A.); curve 5, open combustion chamber, negligible air flow, N.A.C.A. pump (N.A.C.A.); curve 6, open combustion chamber, negligible air flow, earlier N.A.C.A. pump (N.A.C.A.).

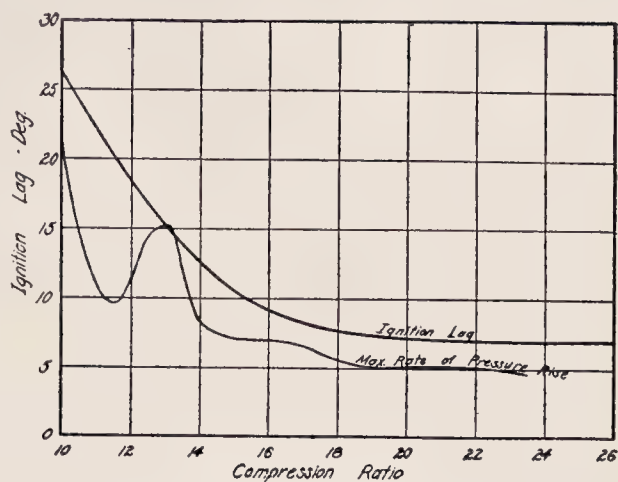


FIG. 7. Effect of compression ratio on ignition lag and maximum rate of pressure rise.

rate of pressure rise. Indeed, if the injection is advanced beyond 17 degrees, the latter effect predominates and the M.R.P.R. falls. If the injection is advanced still farther, the ignition delay period is ahead of the hot top center zone, and consequently the M.R.P.R. increases again because of the excessive ignition lag.

The effect of the injection timing on the M.R.P.R. is complex. It will be noted that the latter jumps suddenly between 12 and 14 degrees before top center, which is the customary injection timing.

Figure 5 refers to a turbulent chamber engine. In nonturbulent engines the variation of the M.R.P.R. with injection timing is still more erratic⁴⁶ (Fig. 11). If M.R.P.R. were used as an index of ignition quality, the injection advance angle would have to be held within close limits.

Of course ignition lag is also affected by the injection timing but to a much lesser degree, as is seen in Fig. 5 and also in Fig. 6, which are reproduced from another paper.⁴⁶ With the normal injection advance the ignition lag is close to its minimum and therefore insensitive to slight variations in timing.

The maximum rate of pressure rise shows a similarly erratic behavior with regard to compression ratio. In Fig. 7 the wavy line is the M.R.P.R. at an arbitrary scale and the heavy line is the ignition lag in degrees crank angle, as they vary when the compression ratio is varied from 10:1 to 24:1, while ignition always takes place at top center. When the compression ratio is about 12:1, three different compression ratios correspond to a single M.R.P.R.

Experiments have shown that the validity of the M.R.P.R. index is also poor. N.A.C.A. tests³⁸ revealed cases where a change in air flow caused ignition lag and combustion knock to decrease

TABLE II

Measurement of ignition lag and M.R.P.R. of the primary standard reference fuels
 24:1 compression ratio; 200°F. intake air temperature; 9 in. of mercury supercharge

Fuel	Cetane number	Ignition lag		M.R.P.R.	Audible knock
		Degrees crank angle	Milliseconds		
Cetane	100	4.8	0.9	21	Very smooth
Alpha-methylnaphthalene	0	8	1.48	25	Very rough
Straight-run Mid-Continent gas oil	55	5	0.93	20	Very smooth

and at the same time the rate of pressure rise to increase. It has also frequently been observed that an increase in intake air pressure or temperature increases the M.R.P.R., although at the same time ignition lag and combustion knock go down.

At extreme conditions the M.R.P.R. index fails to respond. We have measured the ignition lag and M.R.P.R. of the primary standard reference fuels at 24:1 compression ratio, 200°F intake air temperature, and 9 in. of mercury supercharge. The results are tabulated in Table II. The table shows that under conditions that are extremely favorable to combustion the difference between the best and the poorest fuel is still very pronounced to the ear and quite pronounced in ignition delay but fades away in the maximum rate of pressure rise.

Ignition lag is a convenient index of ignition quality when determined with the instrumentation to be described later. The reproducibility of the results is satisfactory if ordinary precaution is exercised. The recent report of the Volunteer Group for Compression-Ignition Fuel Research² showed an average deviation of 1.7 cetane numbers for twelve fuels and twenty-two laboratories using delay methods. This will, no doubt, be further reduced with improved instrumentation.

The validity of the results obtained with the ignition lag method cannot be decided conclusively as yet, but reports available^{6,48,31,37,2} indicate that it is of a high order.

Misfiring is a most convenient ignition index inasmuch as it needs hardly any instrumentation.

It is simple to throttle the intake air on any engine until misfiring occurs. Of course the range of fuels that can be tested in this way is rather narrow, unless the compression ratio is varied. The objection to this type of test is that an engine running a great deal on the borderline of misfiring deposits so much soot that frequent cleaning is necessary. This is obviated by the C.C.R. method, which uses a motored engine and allows

injection only during a few revolutions. The lowest compression ratio at which firing takes place is the ignition index.

There is, however, a certain conflict in the C.C.R. method between convenience and reproducibility. To obtain reproducible results, the heat and the residual gas condition of the engine must be strictly identical. A trial injection, however, upsets the equilibrium, whether it results in firing or not. Therefore an extremely rigorous routine must be maintained which involves considerable loss of time incurred during the waiting periods. These difficulties were greatly relieved by a special injection control device designed by MacGregor,³⁰ which automatically by-passes thirty out of every thirty-two injections.

With regard to validity the record of the misfiring method is better than fair,⁴⁸ but the motored engine seems to be somewhat behind the running engine as far as correlation with the delay rating is concerned. The recent Volunteer Group Report² showed that the C.C.R. ratings were generally 2 to 3 cetane numbers higher than the ratings by the delay method except for the doped fuels which were shown up poorly by the C.C.R. method. Since the cylinder walls are cooler and the ignition lag is nearly 180 degrees, the C.C.R. test may represent starting conditions rather than those of a running engine.

Not much can be said in favor of the "computed combustion knock" in regard to convenience. It involves a laborious evaluation of indicator cards. No data are available to estimate its reproducibility. Its validity is of a high order, according to recent reports,³⁷ as it gives good correlation with ignition lag ratings for both doped and undoped fuels.

C. Physicochemical Methods of Fuel Rating

More space has been given to engine ratings because they alone are considered authentic,

but physicochemical methods of fuel rating are also of interest.

The most popular indices in use are (1) the Diesel index with the formula

Diesel index =

$$(\text{A.P.I. gravity} \times \text{aniline point})/100;$$

(2) the viscosity-gravity index with the formula

$$G = 1.082A - 0.0887$$

$$+ (0.776 - 0.72A) \log \log (KV - 4)$$

where A = viscosity-gravity index, G = specific gravity at 60°F, and KV = kinetic viscosity at 100°F in millistokes; and (3) the boiling point-gravity index with the formula

$$G = A + (68 - 0.703A) \log B.P.$$

where A = boiling point-gravity index, G = A.P.I. gravity at 60°F, and $B.P.$ = 50 per cent distillation point in °C.

The correlation of these chemical indices between themselves and with engine tests has been investigated by Hubner and Murphy,²⁵ Schweitzer and Hetzel,⁴⁷ Yamazaki and Ota,⁵² and the U.S. Naval Experiment Station.³⁷ Applied to petroleum products all three indices give fairly good correlation with engine tests, but they generally fail on doped fuels or oils of vegetable origin. Specifically, the addition of a small per cent of ethyl nitrate increases the cetane number of a 50-cetane fuel about 8 cetane numbers per 1 per cent of ethyl nitrate added,³⁷ but the change in all three chemical indices occurs in the wrong direction.

Nevertheless, the physicochemical indices fill a useful place, as they permit estimation of the ignition quality of the present commercially available fuels from simple physical and chemical data that are either available or can be determined with little trouble. None of the present indices is, however, good enough to take the place of the engine testing when accuracy is essential. Another consideration is that fuels which are now in use may not be typical in the future. The use of dopes, hydrogenation, polymerization, oils of coal and vegetable origin, and other unforeseen developments may so change the Diesel fuel picture that no empirical rating can be relied upon.

V. Development of Testing Technique

The discussion in the foregoing section attempted to explain why the variety of methods available for testing the ignition quality of Diesel fuels has narrowed down to a few alternatives of the engine delay method. All of the methods that

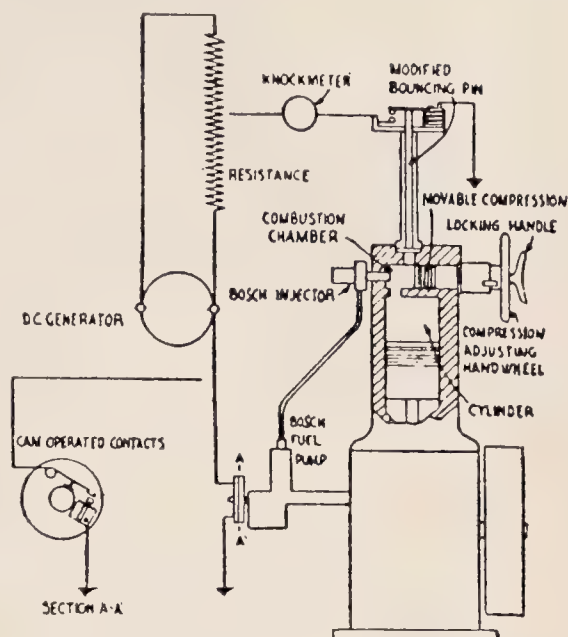


Fig. 8. Schematic circuit used with the knockmeter delay method

enjoy some recognition at present are based on the ignition lag index. The differences are minor and concern technique and instrumentation. A description of four of these methods—the indicator, the knockmeter delay, the Socony-Vacuum, and the Penn State method—is sufficient to cover the field.

(1) *The indicator method* is still the most popular in Europe. The ignition lag is determined from an indicator card on which by a special device the beginning of the injection is marked. The marking device is ordinarily actuated by the needle valve stem. If under identical engine setting the sample fuel gives an ignition lag equal to that of a certain reference blend, the concentration of the high reference fuel is the rating. The reproducibility of the indicator method is about 3 cetane numbers. The chief disadvantage of the method is its inconvenience; it is too laborious for routine testing.

(2) *The knockmeter delay method* has been used predominantly by the Volunteer Group for Compression-Ignition Fuel Research, after the procedure had been worked out, principally by T. B. Rendel. It uses the converted C.F.R. engine and an instrumentation shown schematically in Fig. 8. The apparatus includes a neon lamp which rotates with crank-shaft speed, a contractor actuated by the opening of the nozzle to flash the neon lamp to indicate the time of injection, a protractor to show the angular position of the flash, a modified bouncing pin which rests on a diaphragm in the cylinder head and which upon bouncing separates two contact points and interrupts the flow to the knockmeter,

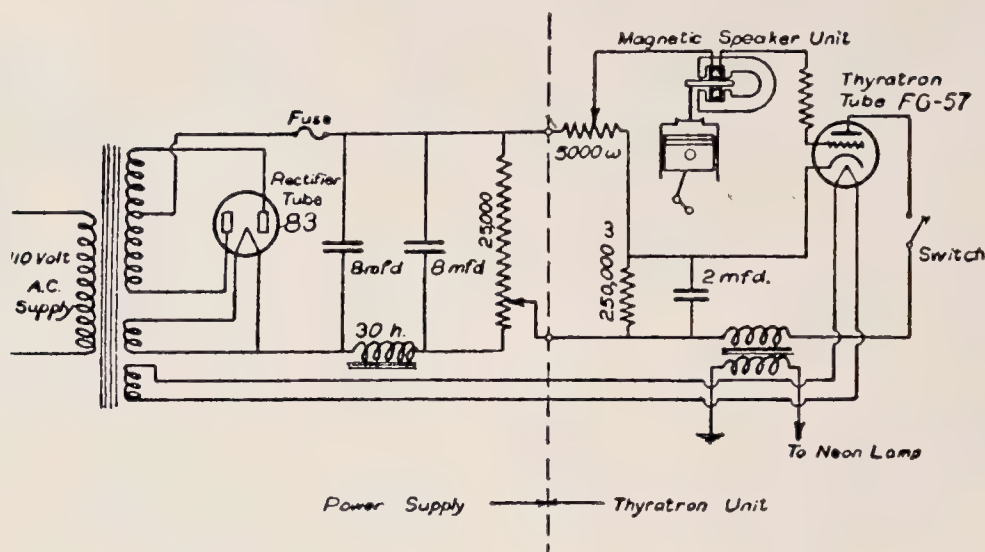


FIG. 9. Circuit of Hetzel and Schweitzer's magnetic pick-up ignition indicator

a knockmeter which is a heavily damped thermocouple type voltmeter, and a mechanical interrupter on the end of the fuel pump shaft to start the flow of current through the knockmeter. A direct current is passed through the interrupter, bouncing pin and knockmeter circuit and the dial indication is read. Two reference fuels, one giving slightly greater and one a slightly smaller knockmeter reading, are found by trial, and the unknown fuel is given a rating by interpolation.

The underlying principle is good. The knockmeter provides a convenient averaging if the injection or ignition points are erratic. In its present form the method is highly standardized; the procedure is printed in Appendix I (see page 331).

The convenience and reproducibility of this method are adversely affected by the use of the bouncing pin. The friction between pin and barrel and the arcing between the contact points causes irregular action, unless a multiplicity of adjustments listed in the procedure is continuously attended to.

The use of the knockmeter is not as advantageous as it might at first seem. The integrating effect is of advantage if there is much spread in the ignition point of the successive cycles as with spark-ignition engines, but in a clean and properly operating Diesel engine the cycles repeat remarkably well and the spread in the ignition point is insignificant. However, the heavily damped knockmeter slows up the testing considerably.⁴⁵ In changing fuels flushing of the line is discouraged because the absence of firing of only a few seconds puts the knockmeter hand off the scale, but with resumed firing equilibrium conditions are resumed very slowly.

In spite of these shortcomings the reproducibility of the knockmeter delay method is quite satisfactory. From the last report of the Volunteer Group² the average deviation of the knockmeter delay ratings was 1.8 cetane numbers. If, nevertheless, the same report recommends that "... the bouncing pin type of instrumentation should be definitely discarded in favor of the balanced diaphragm of the magnetic pick-up type," the recommendation is based more on the inconvenience than on poor reproducibility.

(3) *The Socony-Vacuum method*, devised by C. H. Schlesman, uses a balanced pressure diaphragm in place of the bouncing pin, but otherwise uses the same engine operating conditions as the bouncing pin delay method. The following description is from the report of the Volunteer Group²:

"An insulated contact is placed on the tip of the injector feeler pin. A slight rise of the valve makes a contact which starts an electric current flow. A balanced pressure diaphragm is placed in the bouncing pin hole in the engine head. Pressure on top of the diaphragm is arbitrarily maintained at fifty pounds above compression pressure by connection to a CO₂ bottle. Combustion pressure causes contact to be made which stops the before-mentioned electric current flow. The successive delay times or current times are averaged by means of a special type condenser and a vacuum tube voltmeter. The start of injection is visibly indicated by a neon flasher and flywheel pointer which shows the injection time in degrees on a flywheel protractor for each cycle.

"Details of the apparatus may be obtained from the Socony-Vacuum Oil Corporation. Comments of those who have used the apparatus are very

favorable in regard to ease of handling and the results compare well among themselves and also with averages by the bouncing pin delay method."

While the Socony-Vacuum method is no doubt superior to the knockmeter delay method in convenience, in reproducibility it is a little inferior, showing an average deviation of 2.1 cetane numbers from the "true" values.

(4) *The Penn State method* was devised by Hetzel and Schweitzer.²⁰ In this method the bouncing pin was replaced by an electromagnetic pick-up, such as is used for phonographs and radio speakers of the magnetic type. A short stiff wire resting on the diaphragm transmits the motion of the diaphragm to the armature of the pick-up. The electromotive force generated in the coil surrounding the armature is used to control the operation of a thyatron tube. When the velocity of the diaphragm is high, as at the time of ignition, the thyatron relay trips and causes a neon lamp to flash. The timing of the flash is read on the protractor.

The circuit is shown in Fig. 9. The current generated in the coil reduces the negative voltage on the grid of the thyatron tube, thereby causing it to conduct, and permits a condenser to discharge. The current thus passing to the plate of the tube goes to a coil, which in turn sends a flash through the neon lamp. The neon lamp flashes once in every cycle, at the moment the velocity of the pick-up motion reaches a pre-determined magnitude. At any other time the voltage generated is insufficient to trip the thyatron relay, and the neon lamp remains dark.

A pick-up identical with the one described is mounted on the end of the needle valve stem and indicates the injection. A small neon lamp of the low voltage type is connected to each pick-up and mounted on the fly-wheel, which is provided with a stationary angle scale for reading the position of the neon flashes to an accuracy of 1/10th of a degree.

The mechanism of the pick-up is practically frictionless. No electric contacts are used, and therefore troubles with arcing and pitting are eliminated. The wire and armature have a high natural frequency, so that they follow faithfully the motion impressed upon them. Both pick-ups are claimed to be insensitive to rough handling and to the manner in which they are mounted.

The technique followed in conjunction with the magnetic pick-ups is known as the "fixed ignition lag method." The injection timing is kept at, say, 18 degrees crank angle before top center. Ignition is always to occur at top center exactly. For low cetane fuel the required compression ratio to produce top center ignition (after 18 degrees ignition lag) is high; for high cetane fuels it is low.

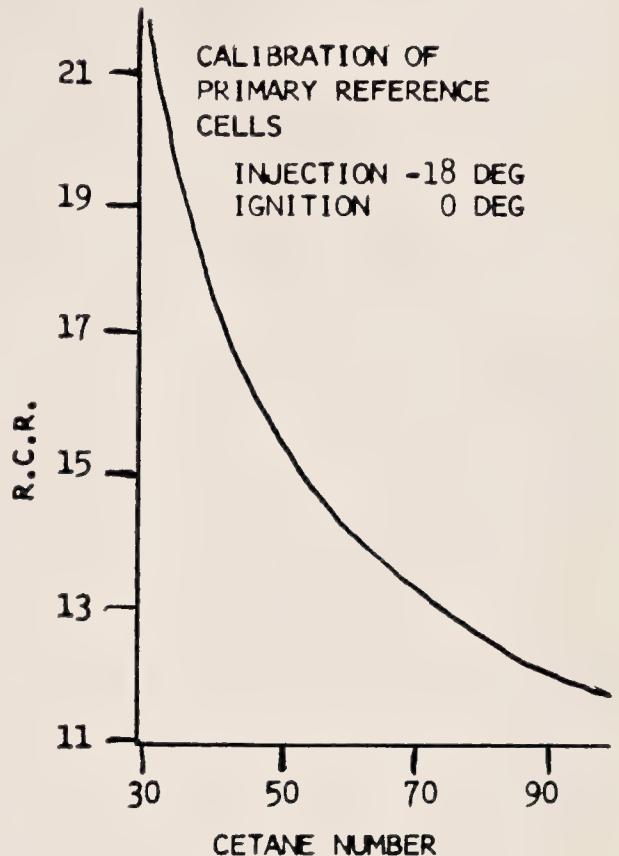


FIG. 10. Calibration curve of the required compression ratio versus cetane number

By moving the adjustable plug the compression ratio is adjusted until the neon lamp indicates ignition at top center.

If the R.C.R. (required compression ratio) of the test fuel is equal to that of the reference blend, the ignition qualities of both are equal. Absolute matching may not be easy to obtain, but the unknown fuel can always be bracketed between two reference fuels and the rating approximated by interpolation.

If a number of samples are to be tested in one day, the use of a calibration curve is economical. By testing a number of the reference blends and noting the R.C.R. for each blend, a curve of R.C.R. versus cetane number is plotted on cross section paper. By determining the R.C.R. of the unknown fuel and marking it on the calibration curve, its cetane number can be read. Figure 10 is a typical calibration curve obtained under the operating conditions listed in Appendix II. For approximate rating a permanent calibration curve can be used. For accurate rating, however, a "day curve" or bracketing is necessary.

The advantages claimed for the Penn State method are the speed and accuracy with which the tests are performed and the simple reliable apparatus which is used. All of the waiting associated with the other methods is eliminated,

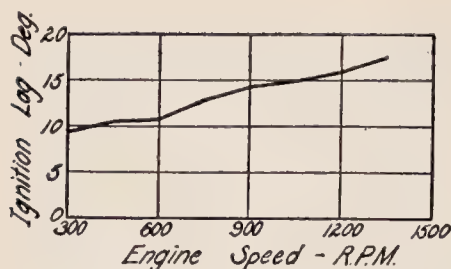


FIG. 11. Effect of engine speed on ignition lag.

so that eight fuels can be rated in an hour, as compared with twelve per day rated by the indicator method⁶ or one per hour rated by the knockmeter method.⁴² The Volunteer Group Report listed the reports of eight laboratories using the Penn State method and its modifications. The average deviation of these from the "true" ratings is calculated as 1.42 cetane numbers, which is less than that of any other method used.

VI. Standardization of Operating Conditions

Although the ignition lag methods are not very sensitive to operating conditions, better reproducibility is attained if the operating conditions are standardized. A list of operating conditions recommended by Hetzel¹⁹ is printed in Appendix II.

In selecting operating conditions under which the tests are to be conducted, the following three requirements should be satisfied as far as possible: (1) the conditions chosen should be typical of usual commercial engine practice, (2) they should be easy to maintain in the test engine, and (3) such values should be chosen that slight variations from the standard value will have a minimum effect on the results of the test.

Figure 11 shows that the effect of engine speed on ignition lag is small and its effect on rating probably negligible. A test speed of 900 rpm. is satisfactory.

Hetzel has found¹⁹ that the effect of jacket water temperature on the ignition lag is quite pronounced, but the ratings obtained with 210°F and 328°F jacket water temperature seldom differed by more than 1 cetane number. A temperature of 210°F is recommended, as it is easy to maintain with evaporative cooling.

Hetzel made a similar observation about the intake air temperature. Ratings obtained with 100°, 150°, and 200°F air temperature seldom differed by more than 1 cetane number. Therefore the Volunteer Group standard of 150°F is acceptable, although higher than is found in practice.

The effect of the lubricating oil temperature has never been investigated.

For ignition point, top center was found highly satisfactory, because it makes ignition pressure rise distinct and easy to identify. Incidentally, with ignition at top center, ignition lag is about minimum (see Fig. 6), therefore a deviation in injection timing will cause minimum deviation in ignition lag. Hetzel investigated the effect of the ignition point (-4° to $+2^{\circ}\text{C}$) on both the ignition lag and rating and found the former to be small and the latter negligible.

For ignition lag Hetzel recommends 18 degrees, as against 11 degrees recommended by the Volunteer Group and 15 degrees recommended by W. G. Ainsley. In the selection the following considerations deserve attention.

The ratings themselves are practically independent of the ignition lag used in the tests performed with the fixed ignition lag method. Hetzel tested sixteen fuels with 10, 12, 14, 16, and 18 degrees ignition lag each. The maximum deviation from the mean was always less than 1 cetane number and the average deviation was only 0.36 cetane number. The disadvantage of the short ignition lag is that low cetane fuels require very high compression ratios for testing. The disadvantage of the 18 degrees ignition lag is that it is longer than the usual ignition lag in commercial engines. Hetzel's compression ratios were, however, unnecessarily high, because he used unnecessarily small injection quantities. More will be said about this later. With the proper injection quantities a standard ignition lag of 15 degrees seems very acceptable. In testing fuels of 30 cetane number or less, the ignition lag may be increased to 18 degrees and the results will still be comparable.

The nozzle valve opening pressure is tied up

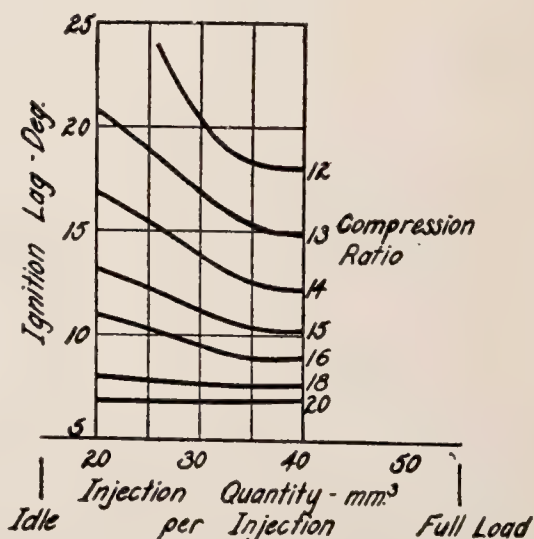


FIG. 12. Effect of injection quantity on ignition lag.

with the nozzle and the injection line. It may be anything between 1200 and 2500 psi, provided the injection is regular. Double injections make testing difficult. Hetzel obtained regular injections with 1300 ± 100 psi with a Bosch nozzle DM30S3 and a $\frac{1}{8}$ -in. \times 25-in.-tube. For a given nozzle and tube the proper opening pressure can be determined by indicating the needle lift with a pick-up and oscillograph. In the range mentioned the ignition lag is independent of the opening pressure.

Fuel quantity injected per cycle has a greater effect on ignition lag than was suspected. Figure 12 shows the relation for a 55 cetane number fuel. Hetzel chose a fuel quantity as small as 20 mm^3 , "because this is sufficient to give regular injections, but is not so much as to produce violent combustion when poor fuels are burned." However, at low compression ratios the ignition lag is very sensitive to the injected fuel quantity, especially if the latter is small. This by itself is a disadvantage. The tentative standard of the Volunteer Group is $13 \text{ cm}^3/\text{min}$ or 29 mm^3 per injection. Figure 12 shows that injection quantity should be increased at least to that amount which would bring it closer to the flat nonsensitive region. It also has the further advantage that it would reduce the required compression

ratio and make the ignition lag standard of 15 degrees more attractive. Of course an increased injection quantity requires more frequent cleaning of the engine.

The potentiometer settings should be such as to give earliest indications of injection and ignition, respectively. In exceptional cases it is possible to obtain "combustion flash" on compression alone, therefore as a precaution the ignition potentiometer setting should be checked so that with injection cut off no flash occurs. With ignition at top center the combustion pressure rise is so rapid that the ignition lag read is almost independent of the potentiometer setting and no precise adjustment is necessary.

VII. Present Status of Diesel Fuel Testing, Technically and Commercially

In this country the working out of a method for testing Diesel fuels on ignition quality is in the hands of the Volunteer Group for Compression-Ignition Fuel Research, in which all major oil companies are represented. Under the chairmanship of T. B. Rendel this organization has worked hard for two years to solve the problem, and it is near to its goal now. It is

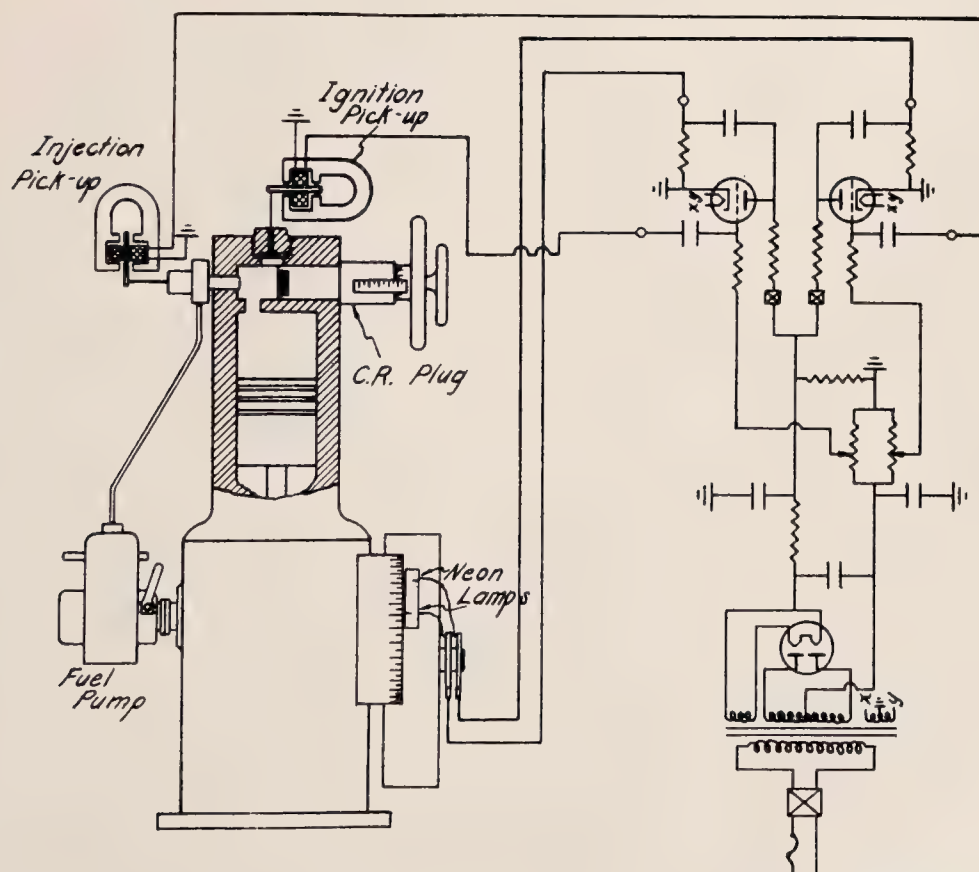


FIG. 13. Schematic wiring diagram of the Aminco-Penn State ignition lag indicator

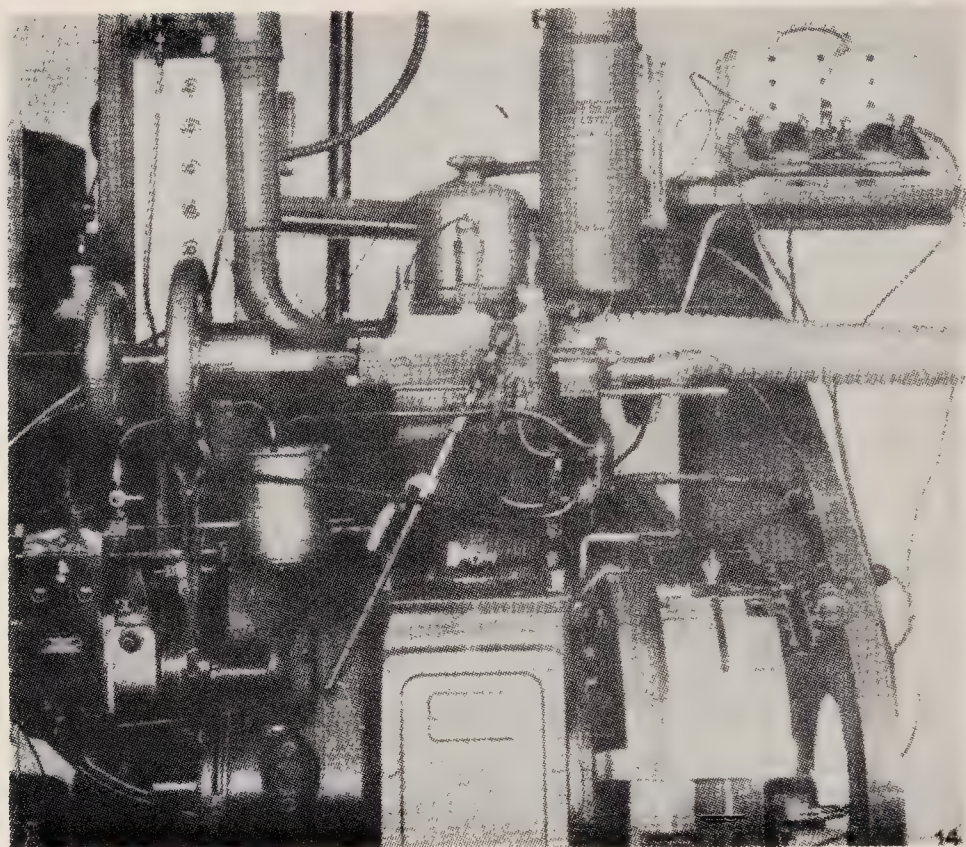


FIG. 14. Aminco-Penn State ignition lag indicator mounted on a C.F.R. Diesel fuel-testing engine.

predicted that within a short time this group will be prepared to submit to the A.S.T.M. a tentative standard for adoption.

There is universal agreement that Diesel fuels be rated for ignition quality in an engine on the basis of their ignition delay and that the rating be expressed in terms of cetane numbers. There is almost universal agreement that the high turbulent Diesel conversion to the C.F.R. engine shall be used for testing. Although the nonturbulent type of engine has an advantage for fuel testing in being more sensitive to ignition quality, this is outweighed by the fact that the popular high-speed Diesel engines in this country are of the turbulent type.

The only item still left open is the exact type of instrumentation, but even therein considerable progress has been made lately. The bouncing pin has been definitely discarded in favor of the balanced diaphragm or magnetic pick-up type of instrumentation. The latter type has been simplified and made more convenient by the American Instrument Company. The American instrument employs the simplified wiring shown in Fig. 13, designed by R. L. Alcorn, Jr., and J. S. Chandler, and an improved protractor in which the injection neon lamp and ignition neon lamp are displaced by 15 degrees (an 18 degree offset can also be used). If the compression ratio

is properly adjusted for the fuel, the two neon flashes appear as a single luminous line.

Figure 14 shows the pick-ups mounted on the C.F.R. engine, while Fig. 15 shows the encased electronic relay, weighing 7.5 lb.

In Europe the Diesel fuel testing is largely in the hands of the Institute of Petroleum Technologists. The Institute agrees with the American Volunteer Group in the principle of engine method based on ignition delay, but leaves open to the tester the choice of engine and the instrumentation. According to the I.P.T. plan the ratings are reported in ignition numbers, obtained by expressing the percentage of the high ignition quality reference fuel in the low ignition quality reference fuel, divided by ten and reporting to the nearest half number. The I.P.T. discourages the use of primary reference fuels (cetene), and favors the use of secondary reference fuels on account of the more consistent results obtained thereby on a variety of types of engines. The Volunteer Group, however, does not consider it practical to adopt secondary reference fuels over a long period of time and favors the use of primary reference fuels such as cetane and alpha-methylnaphthalene.

It is notable that while Diesel fuel testing is more advanced in this country than abroad, in the use of Diesel fuels we are far behind. This

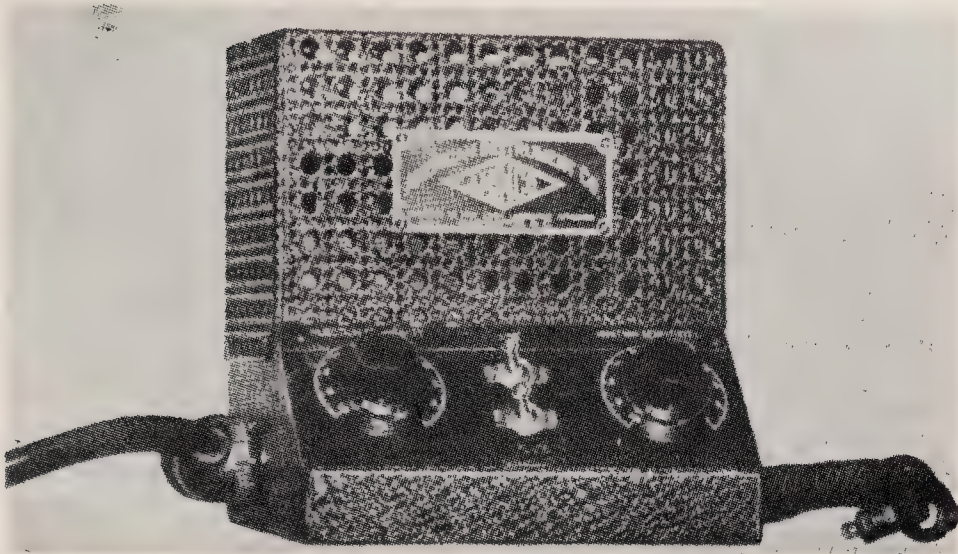


FIG. 15. Electronic relay of the Aminco-Penn State ignition lag indicator

refers to automotive application, especially to trucks and busses.

In England, France, and Germany the majority of large trucks and busses produced in the last couple of years are equipped with Diesel engines, while in this country only a fraction of 1 per cent is so equipped. The chief incentive for the use of the Diesel engine abroad is its economy: the fuel mileage is roughly double, and, furthermore, there is considerable difference in the price of Diesel fuel and gasoline. In this country gasoline is cheap and the introduction of the Diesel engine correspondingly slow. The one exception is the tractor field, where one prominent builder is turning out Diesel tractors at the rate of about a thousand a month.

The present consumption of Diesel fuel in the U.S. is roughly estimated at 30 million barrels per year and is rapidly rising. Under these circumstances the commercial significance of Diesel fuel testing is expected to grow, even if it may not quite reach the commercial significance of the octane rating. The possible introduction of successful Diesel fuel dopes will greatly increase the demands on ignition quality rating.

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Appendix I. Tentative Standard Operating Conditions and Procedure for Delay Period Method of Rating Diesel Fuels

I. Operating Conditions

1. Engine speed.....	900 \pm 3 rpm
2. Cylinder.....	High turbulence variable compression Diesel cylinder
3. Jacket temperature.....	Constant within $\pm 1^\circ\text{F}$; limits 205°-212°F
4. Cooling liquid.....	Distilled water
5. Inlet air temperature.....	150 \pm 2°F
6. Crankcase lubricating oil.....	SAE 30
7. Oil pressure.....	25-30 psi
8. Valve clearance.....	Intake 0.008 in. cold; exhaust 0.010 in. cold
9. Injection advance.....	10° BTDC (constant)
10. Injection pressure.....	1500 \pm 50 psi (opening pressure)
11. Fuel quantity.....	13.0 \pm 0.5 cm ³ /min
12. Injector cooling—water temperature.....	100 \pm 5°F
13. Injector specifications.....	Bosch DN30S3
14. Injection pump specifications.....	Bosch PE1B50A302/3S97, port closing at 0.075" \pm 0.005" lift from base circle

15. Fuel line—tank to pump	$\frac{3}{8}$ " copper tubing
16. Fuel line—pump to injector	$\frac{1}{4}$ " O.D.; $\frac{1}{8}$ " I.D.; length 36 in.
17. Fuel tank height	25" \pm 1" from bottom of tank to pump inlet
18. Knockmeter generator voltage	120 \pm 1 volts

II. Procedure

A. Starting and Stopping The Engine

While the engine is being turned over by the electric motor, the fuel by-pass valve on the injector is closed, and the compression ratio is increased until the engine begins to fire.

To stop the engine, the fuel by-pass valve on the injector is opened and the electric motor then switched off.

B. Checking Injection Pump for Port Closing

The pump plunger port should close when the plunger has traveled up $0.075'' \pm 0.005''$ from the base circle of the cam. This setting is important, as it influences the injection rate. To check the port closing see Paragraph 14 under "Installation Instructions." This adjustment is made in the factory and should not require resetting unless it has been tampered with.

C. Injection Pressure Setting

Remove injection pump cover and with injection line pressure gauge connected and injector arranged to spray into the air operate the pump plunger with a screw driver used as a lever. With the pressure gauge set at 1500 psi adjust the pressure on the injector spring until equal quantities of fuel spray from the gauge and injector. The opening pressure of the injector will then be the same as indicated on the gauge.

D. Injector Indicator Setting

1. Loosen the contact spring carrier clamp nuts and adjust until the spring leaf just touches the injector pin. Then set the clamp nuts to provide one-half turn initial tension on the spring.

2. Adjust the gap between the contact points to $0.004''$.

E. Bouncing Pin Preliminary Static Setting

Make static bouncing pin setting as follows:

1. Set gap between pin and arm $0.005''$ with gap adjusting screw.

2. Bear down lightly on the end of the contact arm spring so that the arm is held on its seat. Adjust the spring tension screw until the screw just touches the spring. Then increase the tension by turning the screw down five notches.

F. Final Compression Ratio and Bouncing Pin Adjustment

After the engine has reached equilibrium the compression ratio and bouncing pin setting at which an unknown fuel is rated are determined as follows:

1. Adjust the compression ratio about two compression ratios above that at which definite misfiring occurs.

2. With the engine firing, close the bouncing pin gap between pin and arm by turning the adjustment screw up until two distinct lines appear ahead of the "bump" on the optical indicator diagram. (This indicates that the bouncing pin arm is deflected by the compression pressure before combustion.)

3. With the engine firing, increase the bouncing pin gap between pin and arm by turning the adjustment screw down until the double line on the optical indicator just coincides with the base line. (This indicates that the bouncing pin arm is not moved by compression pressure, but is deflected the moment compression pressure is exceeded by combustion.)

4. Observe the angle at which combustion starts. The correct angle of combustion for making a rating is 1° after top dead center. Readjust compression ratio until this condition is obtained.

5. After a change in compression ratio, readjust the bouncing pin as outlined in Paragraphs 2 and 3 above.

6. If the indicated angle of injection after the final bouncing pin setting has shifted more than $\frac{1}{2}^\circ$, readjust the compression ratio and pin as outlined above.

7. Check the regularity of the bouncing pin on the neon tube indicator. If the angle of combustion fluctuates more than $\pm 1^\circ$, adjust the bouncing pin tension screw by trial until steady readings are obtained.

G. Adjustment of Contact Breaker

The make and break points in the knockmeter circuit should be adjusted for an 8° contact period, as determined on the neon tube indicator. This can also be indicated on the knockmeter and should produce a reading of 80 to 100 on the scale when the generator voltage is 120 and the engine is not firing. The breaker timing should be adjusted to make contact approximately 2° before top dead center as indicated on the neon

tube indicator. Check this setting on the knockmeter with 120 generator voltage. A knockmeter reading of 50 should be obtained with the engine firing when combustion occurs at 1° after top dead center. Advance or retard the breaker until such a knockmeter reading is obtained.

H. Cetane Number Determination

The cetane number of a fuel is ascertained by comparing the delay (as measured with the knockmeter) for the fuel with those for various blends of the reference fuels until two blends differing in delay by not more than the equivalent of 8 cetane numbers are found, one of which has a longer delay and the other a shorter delay period than the sample. The reference fuel which would exactly match the sample is computed by interpolation from the knockmeter scale readings of the fuels.

An alternate series of knockmeter readings is taken on the test fuel and reference fuel blends. After changing from one fuel to the other, 5 minutes must be allowed to insure the complete change over, since there is a comparatively large volume of fuel in the pump and line.

At least three alternate series of readings should be taken on each fuel, and if the average knockmeter reading of the fuel sample is higher than that of the reference fuel blend, the test should be repeated with a blend containing decreased proportion of the high cetane number

of reference fuel. The test is continued in this manner until the knockmeter reading for the sample is definitely higher than for one blend and lower than for another blend of the reference fuels.

I. Precision of Results

The cetane number should be reported in the nearest whole number to the exact rating as computed by interpolation from the knockmeter readings.

J. Miscellaneous Notes and Suggestions

1. *Clean* fuel must be used. It is suggested that the fuel be filtered through thin chamois leather into the fuel tanks.
2. The fuel lines and fuel pump must be thoroughly flushed of air before starting the engine. After the engine is running better results are obtained by switching quickly from one fuel to another *without flushing the fuel pump*, and allowing 5 minutes for the change over.
3. When changing fuels in the tanks, it is very necessary to flush thoroughly the line to the switch valve until a solid fuel stream is obtained from the bleed drain.
4. The fuel injection timing should be shown continually on the spark quadrant and any deviation from 10° before top dead center must be corrected before each knockmeter reading is taken.

Appendix II. Recommended Procedure for Diesel Fuel Testing by the Fixed Ignition Lag Method

I. Operating Conditions

1. Engine speed.....	900 ± 30 rpm
2. Jacket temperature.....	Boiling point of water constant within ±1°F
3. Inlet air temperature.....	150 ± 0.5°F
4. Lubrication oil temperature.....	150 ± 10°F
5. Injection advance.....	18 deg. B.T.C.
6. Ignition.....	At top center exactly
7. Nozzle opening pressure*.....	1300 ± 100 psi
8. Fuel quantity.....	0.020 cm³ per injector ± 10 per cent
9. Potentiometer.....	To give earliest indication of injection and ignition, respectively

* For Bosch nozzle DN30S3 and a 1/16-in.- × 25 in.-tube. If a different nozzle or tube is used the injection pressure should be so chosen as to give uniform injections with a sharp beginning and a single principal opening.

II. Procedure

1. The engine is motored for approximately 5 minutes while the air and water heaters and the thyatron tube warm up.
2. The by-pass valve in the nozzle is then closed, the injection timing adjusted, and the

compression ratio set to give reasonably smooth running while the engine warms up. The engine should run under power for at least 20 minutes in order to attain equilibrium temperature conditions of the engine and of the crankcase oil.

3. Injection timing is adjusted by the pump timer until the neon lamp flashes at 18 degrees

before top center. The ignition indicator is then switched on, and the compression ratio is varied until the neon flash indicates ignition at top center. The scale reading of the compression ratio adjusting plug is then recorded. Following that, the compression ratio is increased until ignition takes place several degrees before top center, and again decreased until ignition is indicated at top center and the scale reading of the compression ratio adjusting plug is again recorded. This is repeated so that altogether two determinations are made with increasing and two with decreasing compression ratios. The average of the four readings is then used to determine the required compression ratio for that fuel. The R.C.R. is calculated by the formula $R.C.R. = 1 + 18/H$, where H is the average of the four micrometer readings of the adjustable plug.

4. When switching from one fuel to another, the pump suction space is flushed for approximately 5 sec, then, while the injection tube and

nozzle are being purged of the fuel previously used, the other tank is drained, flushed, and filled with the next fuel to be tested.

5. After testing a series of blends of the two reference fuels, the volumetric percentage of the high cetane fuel in the low cetane fuel is plotted against the corresponding R.C.R. values. The R.C.R. of the sample fuel is placed on the curve which determines the rating of the sample fuel. If the sample fuels are tested first, the R.C.R. of some of the reference blends which are outside of the range of the sample fuels need not be determined. If the approximate ratings of the fuels are known in advance, the preferred procedure is to test the fuels, including the reference fuels, in the order of their ignition quality. This combines the good features of bracketing, with curvilinear interpolation, and also directly compares fuels of similar or identical ignition quality so that relative merit may be more surely ascertained.

Discussion

T. B. RENDEL (*Shell Petroleum Corporation, Wood River, Illinois*): Three years ago a small group, known as the Volunteer Group for Compression-Ignition Fuel Research, was formed to study and eventually to standardize a method for rating the ignition quality of Diesel fuels. This group has pursued its work actively and has submitted three reports. The most recent of these reports was presented to the Society of Automotive Engineers and the American Society for Testing Materials, giving the results of the past eighteen months' work. In this report it is concluded that results of the past eighteen months' work indicate fairly definitely that a direct matching method on the basis of ignition delay is the best from the point of view of reproducibility and validity, and that therefore some sacrifice in simplicity and speed of testing must be made. In this connection it is to be remembered that the octane number test, after several years of development and with a far greater commercial incentive behind it, sometimes requires about 45 min for determination and is still liable to errors of 1 or 2 octane numbers.

Progress in methods of instrumentation has advanced considerably. It is recommended that the

bouncing pin type of instrumentation should be definitely discarded in favor of the balanced diaphragm or the magnetic pick-up type. Further work in a larger number of laboratories is desirable before definitely standardizing on this point. The cetane number is, however, not apparently affected outside the limit of error of the determination.

It is therefore recommended that Diesel fuel be rated for ignition quality on the basis of its cetane number, as determined by an ignition delay method on the high turbulent Diesel conversion of the C.F.R. engine, the exact type of instrumentation for recording the delay to be left to the option of the user pending further work of the Volunteer Group.

The Volunteer Group has investigated Professor Schweitzer's mechanical pick-up type of instrument and is favorably impressed with its operation; cooperative work is now in hand with this instrument. Work is also planned on the correlation with actual service engines. In this connection, it is very encouraging to note that cetane rating is apparently insensitive to the type of engine and operating conditions, which in turn indicates that correlation with service engines is not far off.

THE KNOCK RATING OF MOTOR FUELS

H. W. BEST

Department of Mechanical Engineering, Yale University, New Haven, Connecticut

The knock rating of a fuel is essentially a direct comparison of the intensity of the knock produced by it with that of a standard fuel, these intensities being measured according to a specified procedure. Other methods, such as chemical analysis or bomb explosions, have been found to be inadequate for predicting the knock characteristics of a fuel when in actual service.

The fuels used as a standard of comparison are normal heptane and isooctane (2,2,4-trimethylpentane), first proposed by Edgar.⁶ These fuels are pure hydrocarbons and thus can always be duplicated; they are similar to each other and to gasolines in their physical and chemical properties, and when blended can duplicate the range of antiknock qualities of gasolines likely to be used for motor cars, since isooctane is considerably better and normal heptane poorer in this respect than ordinary motor fuels. Thus blends of these substances establish a standard scale for comparison of any motor gasoline.

In order that the results of different laboratories may correlate, not only is a standard reference fuel necessary, but the engine and the operating procedure must be standardized, because operating conditions affect the relative knock intensities of fuels. Therefore, the Cooperative Fuel Research, single-cylinder, variable compression, vapor-cooled engine was designed specifically for this purpose. In order to obtain the knock rating of a fuel this engine is operated at 900 rpm with a mixture temperature of 300°F and the knock intensity of the fuel measured.¹ The blend of normal heptane and isooctane which matches the fuel in knock intensity under the same operating conditions is then determined, and the fuel is said to have an octane number which is the percentage of isooctane in the isooctane-heptane mixture which it matched.

A specified knock intensity is used which is obtained by varying the compression ratio and is measured by means of a bouncing pin. Secondary reference fuels which have been suitably calibrated against normal heptane and isooctane blends are generally used instead of the expensive primary reference fuels. This method was developed by the Cooperative Fuel Research Committee, on which are represented the Automotive Industry, the Petroleum Industry, and the National Bureau of Standards, and is the result of a great deal of coöperative work done by individual laboratories throughout the world.

In 1932, the Committee had developed the octane number scale, the knock-testing engine, and a procedure. The procedure at that time

differed from the present procedure in that the engine was operated at 600 rpm instead of 900 rpm and the mixture temperature was approximately room temperature instead of 300°F. Also the spark timing was retarded 3.5 degrees with respect to that now in use. This method, now called the C.F.R. research method, was modified because results obtained with it did not correlate with results obtained in service.

Road Ratings

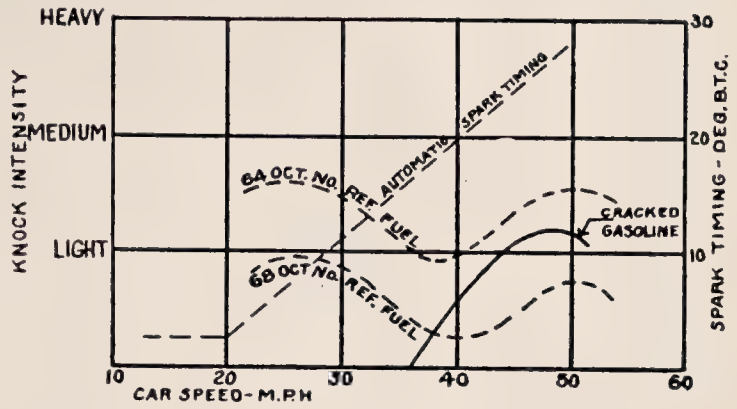
In order to determine what effect actual service conditions have on the knocking characteristics of representative fuels, the C.F.R. Committee conducted in 1932 and again in 1934 comprehensive cooperative road tests at Uniontown, Pennsylvania.^{11,10} A method of rating fuels on the road was developed which consists essentially in comparing the maximum knock intensity obtained with the fuel under test to the maximum knock intensity of reference fuel blends, irrespective of the speeds at which they occur. This method differs from that used in the laboratory in that the comparison of knock intensity is not made at any predetermined speed and the intensity is measured by ear rather than by instrument.

These road tests definitely established the fact that the variations in design of different makes of engine or even differences in adjustments in cars of the same make and model were sufficient to cause considerable differences in the relative knock intensities of fuels of different types. It was found that a cracked fuel, when run in one car, might knock with an intensity which was equal to that obtained with a reference fuel blend differing by 8 octane numbers from the blend it equalled when run in another car. Such differences were found even in two cars of the same make and model, showing that major variations in design were not necessarily the cause of these differences.

The knock intensity of any fuel varies with engine speed, but this characteristic is not the same for different fuels in the same engine or for the same fuel when used in different engines. With one fuel it may decrease continuously with increasing speeds, with another it may reach a maximum value at relatively high speeds or it may reach a maximum at two speeds.

Campbell, Lovell, and Boyd have obtained data which clearly illustrate these differences in knocking characteristics and which are reproduced in Figs. 1 and 2.⁵ They ran a 100 per

FIG. 1. Knocking characteristics of two types of fuels in a 1934 car (Campbell Lovell, and Boyd, Ref. 5).



cent cracked fuel and blends of straight-run reference fuels in a 1934 production car, having an ell-head engine with standard spark timing. These data are represented in Fig. 1, which shows that the reference fuels knocked throughout the speed range, the maximum intensity occurring at about 25 miles per hour and again at 50 miles per hour. The cracked fuel produced the maximum knock intensity at 50 miles per hour, but none at all below 35 miles per hour. The maximum knock equalled that of a 66 octane number reference fuel.

The automatic spark advance was then modified by advancing it 6° at low speeds and retarding it at high speeds with the results shown in Fig. 2. With this change, maximum knock with the cracked fuel occurred at between 25 and 30 miles per hour instead of at 50 miles per hour, and the intensity was decreased slightly. The reference fuels gave a continuous and rapid decrease of knock intensity with increasing speeds, but a 77 octane number blend now knocked with an intensity which equalled that previously obtained with a 68 octane number blend. The cracked fuel equalled in intensity of knock approximately an 80 octane number blend, whereas with the standard spark adjustment it equalled a 66 octane number reference fuel blend. Thus this modification in spark timing in this particular engine caused the fuels to knock at lower speeds; it had but little effect on

the knock intensity of the cracked fuel and considerably increased the knock intensity of the straight-run reference fuels, thus increasing the road knock rating of the former from 66 to 80 octane number. Therefore, the road rating of this fuel was changed by approximately 14 octane units because of the comparatively large effect on the reference fuels.

This example clearly illustrates the effect a change in adjustment of an engine may have on fuels of different types. In Table I are tabulated some of the data obtained at Uniontown showing the effect of different representative engines.¹¹ Column 3 gives the octane number of the straight-run reference fuels which were required for knock-free operation above 15 miles per hour. Column 4 gives the knock intensity obtained with a 100 per cent experimental cracked fuel when used in the same cars. Column 5 gives the knock intensity obtained with a commercial fuel, and columns 6 and 7 give the road ratings of these fuels in each car in terms of octane number of the reference fuel blends which they matched.

A study of this table shows that the reference fuels knocked with the same intensity in Cars 1, 2, 3, and 4, but the cracked fuel knocked considerably more in Cars 3 and 4 than in 1 and 2. Therefore, its rating was reduced from about 76 to 64, when run in the two latter cars. When run in Car 5 this same cracked fuel knocked with approximately the same intensity as it did in

FIG. 2. Knocking characteristics of car represented in Fig. 1 with modified automatic spark timing (Campbell, Lovell, and Boyd, Ref. 5).

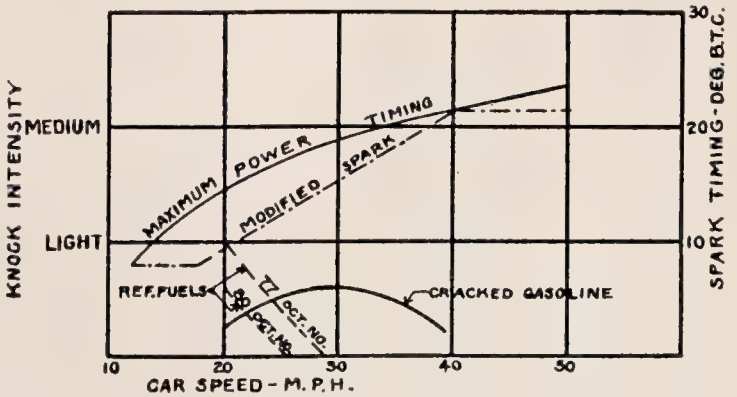


TABLE I

Data obtained with different engines

Car No.	Type of engine	Octane requirement (Reference fuels)	Knock intensity		Road rating	
			Experimen- tal cracked fuel	Commerical fuel	Experimen- tal cracked fuel	Commercial fuel
1	Overhead valve	76-78	Trace	Trace	75	76
2	Ell-head	76-78	Trace	Trace	77	76
3	Ell-head	76-78	Heavy	Trace	64	76
4	Ell-head	76-78	Heavy		64	
5	Ell-head	66-68	Heavy		55	

Cars 3 and 4. However, the reference fuels knocked considerably less in Car 5. Thus the rating was still further reduced to 55, because in this case the reference fuel was affected but not the cracked fuel.

The data in Column 3 indicate that Cars 1, 2, 3, and 4 require a better fuel than does car 5 if the fuel is of the same type as the reference fuel. However, if the cracked fuel is used, Car 5 requires a better fuel than do Cars 1 and 2.

The examples cited above are extreme cases illustrating how different conditions affect the relative knock characteristics of fuels of different types. Such large differences are not common. The maximum differences observed during the Uniontown tests with typical commercial fuels were the equivalent of 5 to 8 octane numbers.

Since two fuels which are alike when run in one engine may vary considerably in another, it is obvious that no single laboratory procedure can be made to give results which correlate exactly with results obtained under the variety of conditions to which any motor fuel is subjected in service. Therefore the average of the road ratings obtained on each fuel during the Uniontown tests was considered the road rating of that fuel, and the laboratory method was made to result in ratings which correlated with these average road ratings.

It was found that the laboratory procedure in use prior to 1933 gave results which were generally higher than the average road ratings.¹¹ With commercial fuels this discrepancy amounted to the equivalent of about 3 octane numbers, the maximum being 5 octane numbers. In the case of a 100 per cent experimental cracked fuel it was 9 octane numbers. By changing some of the laboratory engine operating conditions very good correlation with average road ratings was brought about, the principal changes being an increase in speed from 600 to 900 rpm, an increase in mix-

ture temperature from approximately room temperature to 300°F, and an advance in spark timing of 3.5 degrees. These changes resulted in the present A.S.T.M. Tentative Method of Test for Knock Characteristics of Motor Fuels (Designation D 357-36T), sometimes called the motor method.

Fuel "Sensitivity"

Although the old procedure, now known as the research method, was displaced as a means for obtaining knock ratings for commercial purposes, it was retained for research purposes. By rating a fuel by both methods the susceptibility of that fuel to the changes in operating conditions introduced, as compared to that of the reference fuels, can be determined. For example, if a fuel has the same rating by both methods its knock intensity changed the same as did that of the reference fuel; if its rating differs, then the operating variables have affected its knock intensity more or less than they did the reference fuel. The difference between the ratings of a fuel obtained by the research method and the motor method has been called the "sensitivity" of that fuel.^{10,2} The data obtained in the Uniontown tests show that those fuels having the greatest "sensitivity" as measured by the difference between the research method rating and the A.S.T.M. rating also gave the greatest differences when rated on the road. This indicates that the changes introduced in the laboratory engine operating conditions have an effect which is similar to the changes encountered in service.

Although a change in operating conditions changes the rating of a fuel, whether in the laboratory or on the road, this does not necessarily mean that the fuel is sensitive to that change in regard to knock, for it may be the reference fuel which is sensitive. For example,

from the data obtained by Campbell, Lovell, and Boyd⁵ (Figs. 1 and 2), it appears that the change in spark timing caused no appreciable difference in the knock intensity of the cracked fuel but did considerably increase the knock intensity of the reference fuel. Therefore, in this particular case a considerable change in rating was caused by an engine variable because the reference fuel was sensitive to this variable in regard to intensity of knock, whereas the fuel under test was comparatively insensitive. To determine whether, in general, the differences obtained in rating fuels on the road are due largely to the susceptibility of the reference fuels under test to the changes in operating conditions requires further investigation.

The "sensitivity" of a fuel, as defined by the difference between the research method of rating and the motor method, is determined principally by changing the engine speed and the mixture temperature of the knock-testing engine. The effect of each of these variables is shown diagrammatically in Figs. 3 and 4. As shown in Fig. 3, increasing the speed of the C.F.R. engine usually reduces the knock intensity of fuels. If a given increase in speed reduces the knock intensity of a fuel less than it does that of the reference fuel, then the rating of that fuel will be less at the higher temperature. Therefore a fuel which rates lower by the motor method than it does by the research method may do so because it is comparatively sensitive to a change in mixture temperature and/or insensitive to a change in speed. Thus "sensitivity," as determined by the difference between the research method of rating and the A.S.T.M. or motor method, is a measure

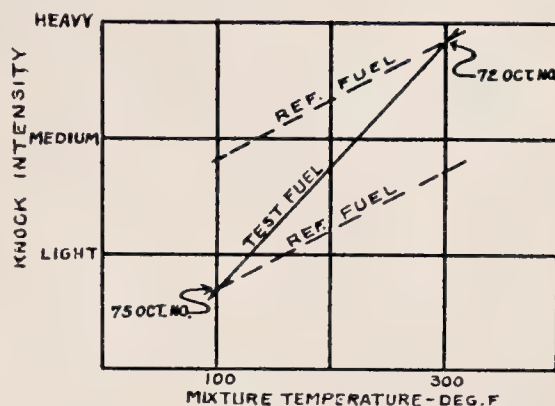


FIG. 4. Effect of mixture temperature on knock intensity.

of the *relative* susceptibility of a fuel to changes in operating conditions, but is not necessarily a measure of the degree to which a fuel responds in knock intensity to such change.

Factors Affecting Laboratory Knock Rating

Since an essential factor in insuring the continued validity of the method of knock rating is the maintenance of correlation with service conditions, and since the present method was designed to correlate with the average performance in service of motor fuels in 1932 model cars, modifications in the method may be necessary from time to time because of changes occurring in motor fuels and engine designs. The road tests conducted by the C.F.R. Committee in 1934 showed that the changes made since 1932, when the method was developed, were not sufficient to warrant any modification.¹⁰ However, preliminary tests with present-day automobiles indicate that some modification in laboratory procedure is now necessary in order that knock ratings may correlate with average current service conditions. It therefore is pertinent to discuss some of the factors which might readily be changed in the laboratory procedure to produce a change in ratings.

It is well known that there are many variables which affect the knock intensity of a fuel when burnt in an engine. Some of these are differences in design, such as combustion chamber shape or material, compression ratio, and spark plug location; others are variations in operating conditions, such as engine speed, carbon accumulation, atmospheric conditions, mixture temperature, spark advance, and mixture ratios. If these factors had the same effect on the knock intensity of all types of fuels, then they would have no effect on knock ratings. However, these factors change the knock intensity of different types of fuels in varying degrees and therefore

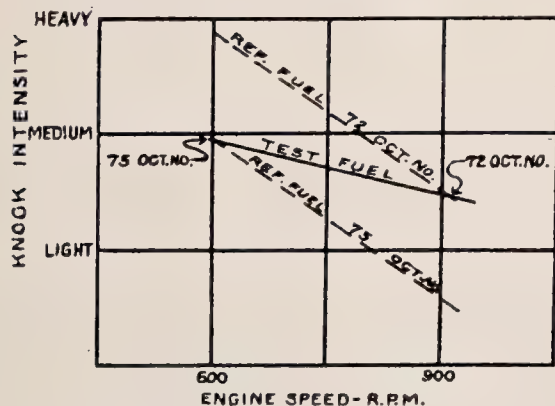


FIG. 3. Effect of speed on knock intensity.

TABLE II

Fuel ratings by two methods and effect of decrease in manifold temperature on octane number

Fuel	Motor method	Research method	Motor method — research method (Col. 3 — Col. 2)	Increase in octane number per 100°F decrease in manifold temperature
1. 100 per cent cracked.....	70.7	79.9	9.2	2.9
2. California straight-run.....	71.9	73.0	1.1	0.5
3. Cracked gasoline + tetraethyl lead.....	74.3	78.8	4.5	2.7
4. Cracked + straight-run + lead tetraethyl...	70.8	74.9	4.1	2.4
5. Cracked + straight-run.....	64.3	67.6	3.3	1.9

anything which affects the detonation of a fuel may affect its rating.

Two of these factors, namely, engine speed and mixture temperature, have already been briefly discussed. Some specific data showing the effect of mixture temperature on ratings were obtained by the C.F.R. Committee.⁸ The fifteen fuels used in the 1934 Uniontown road tests were rated by twenty laboratories at mixture temperatures of 300°, 275°, 250°, and 200°F. In all other respects the procedure used was the motor method. It was found that antiknock values increase directly with decrease in manifold temperatures and that the mean antiknock value of all the fuels tested rose 2 octane numbers for each 100°F drop in manifold temperature.

In Table II are listed for five of the fuels tested approximately the difference between the research and the motor method ratings and the increase in octane number occasioned by a decrease of 100°F in the manifold temperature. The maximum increase was 2.9 octane numbers for a 100°F decrease in temperature and occurred with a 100 per cent cracked fuel which was also the most “sensitive” of all the fuels tested, as determined by the difference between the research and motor method ratings. However, the next most “sensitive” fuel gave very nearly the same decrease, although the difference between the research method and motor method ratings was only slightly over one-half that of the other fuel. This perhaps indicates that the comparatively large difference between the research and motor method ratings of the first fuel was caused largely by the change in engine speed, and serves to illustrate further that the difference obtained by the two methods of rating is not necessarily indicative of the response of a fuel to a change in operating conditions.

It is a well-known fact that spark advance

affects detonation, and, since the effect is dissimilar on different types of fuel, knock ratings may vary with spark timing. Figure 5 shows the effect of spark timing on the knock intensity of three fuels. These data were obtained by Campbell, Lovell, and Boyd, using a single-cylinder engine running at 600 rpm.⁴ It can be seen that at a 40-degree spark advance Fuels 2 and 3 are alike, whereas with the spark retarded to 20 degrees before top center Fuels 1 and 2 are alike. Therefore the ratings of these fuels would depend on the spark timing used.

The A.S.T.M. procedure specifies a spark timing of 26 degrees before top center when the

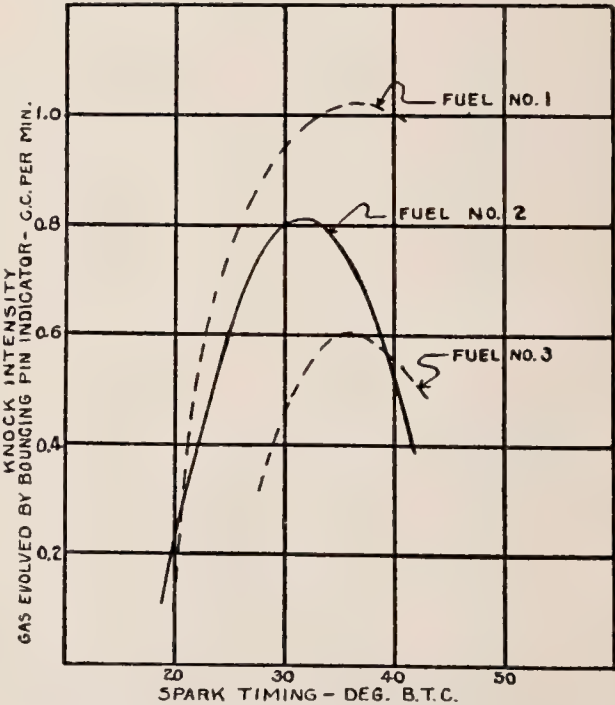


FIG. 5. Effect of spark timing on knock intensity (Campbell, Lovell and Boyd, Ref. 5).

compression ratio is 5 to 1. This timing is automatically changed with compression ratio by means of a suitable linkage. The effect of changes in this timing and its relation to maximum power and maximum knock intensity at different compression ratios is now being studied by the C.F.R. Committee.

There are many other variables which affect knock and therefore might be used to change knock ratings appreciably. However, the three discussed above, namely, engine speed, mixture temperature, and spark timing, are easily controlled and can be readily varied without necessitating any radical change in engine design or procedure. They can again be used, either singly or in combination, to effect a modification in procedure in order to obtain better correlation with average present-day road ratings. However, as pointed out above, they cannot produce exact correlation with all service conditions nor do they take care of all of the factors involved such as, for instance, the volatility and distribution effects.

Campbell, Lovell, and Boyd have presented evidence that in certain cases volatility, as well as chemical composition, may affect the knocking characteristics of a fuel.⁵ Because the fuel entering the cylinders of an automobile engine is only partially vaporized, the quality of the mixture delivered to different cylinders or even to any one cylinder during successive cycles is not uniform. Since the average mixture delivered by the carburetor is generally richer than that producing maximum knock intensity, it is likely that most of the knock occurring in an engine originates from the leaner charges, which are probably richer in the more volatile constituents than the original fuel. If the fuel contains a comparatively large proportion of a relatively volatile fuel which is a knock suppressor, such as benzene, then the knock from these lean charges will be reduced, thus diminishing the knock produced by the engine.

In order to confirm this theory, two fuels were prepared which had the same knock rating by the A.S.T.M. method. One of these fuels was a blend

of benzene and a straight-run fuel, the other was a blend of ethyl ether and a straight-run fuel. Both benzene and ethyl ether are of high volatility, and the former is a knock suppressor whereas the latter is a knock inducer. As was expected, when these fuels were compared in a car on the road, the ethyl ether blend produced a knock of light to medium intensity, whereas the benzene blend produced no knock at all, although they gave the same knock intensity when run in the single-cylinder laboratory engine where the distribution effects were not present.

Factors Affecting Precision of Ratings

There are also variables which at present are not controlled or perhaps not sufficiently so, which may affect the reproducibility of ratings. In order to determine the precision of knock ratings, a group of twenty laboratories, called the exchange group, was formed by the C.F.R. Committee. Three fuels are sent every month to each of these laboratories to be rated. D.B. Brooks, of the National Bureau of Standards, has analyzed 1882 tests on 95 fuels made by this group for the C.F.R. Committee.³ He found the probable error of knock rating to be 0.465 octane unit. Of these 1882 tests, 86.9 per cent showed deviations from the average of less than 1 octane unit, 11.9 per cent between 1.0 and 1.9 units, 1.1 per cent between 2.0 and 2.9 units, and 0.1 per cent over 2.9 units. The types of fuels used were as follows: straight-run fuel with and without lead tetraethyl; aviation fuel with and without lead tetraethyl; straight-run fuel plus cracked fuel; straight-run fuel plus cracked fuel with lead tetraethyl; 100 per cent cracked fuel; two benzene blends; two reference fuels. Of these the 100 per cent cracked fuel showed a distinctly larger error than the others.

The two reference fuels were sent out as test fuels and so were rated against themselves without the knowledge of the operator. Therefore any errors obtained with these fuels were due to experimental errors rather than variations in conditions. If the ratings of these two fuels are

TABLE III

Change in octane number for carbon accumulation due to 100-hour operation

Fuel	Average change	Greatest change	
Straight-run (plus lead tetraethyl)	+0.05	+2.0	-0.8
Straight-run (plus cracked)	-0.3	+0.1	-1.2
Straight-run cracked + lead tetraethyl	-0.8	+1.1	-1.2
100 per cent cracked	-1.2	+0.1	-2.6

assumed to be representative, then perfect technique would reduce the probable error from 0.465 to about 0.25 octane unit.

The factors, other than experimental error, to which these deviations were attributed, were humidity, knock intensity, and carbon accumulation.

The effect of carbon accumulation as determined by these tests is presented in Table II. These data indicate that fuels containing cracked gasoline respond to carbon accumulation, showing a lower octane number on engines run over 100 hr without cleaning than do the other types of fuel.

It is well known that humidity affects detonation, increasing humidity decreasing the knock. Its effect on knock ratings is being studied by the C.F.R. Committee, and the results of some tests to determine this effect have been reported by MacGregor.⁹ He found that the reduction in knock intensity for a given increase in humidity was approximately the same for a straight-run, secondary reference fuel blend, a benzene blend, and a cracked fuel, all of about 68 octane number. Thus a change in humidity would not affect the rating of these fuels when matched against the secondary reference fuels. However, the effect on knock intensity of an increase in humidity was considerably less with a blend of 67.5 per cent octane and 32.5 per cent heptane and considerably more with a straight-run secondary reference fuel blend containing 2.2 cm³ of lead tetraethyl. Thus, if octane-heptane blends were used as reference fuels, the ratings of all the other fuels would be affected. An increase in humidity from 0.002 to 0.023 lb. of water per pound of dry air was estimated to affect the leaded reference fuel approximately 5.7 octane units when matched against octane-heptane blends, and 3.6 octane units when matched against the unleaded secondary reference fuels.

In order to determine whether more rigid specifications regarding the knock intensity at which to rate fuels would result in improved precision, the C.F.R. Committee is also investigating this factor. At present, this is specified in the procedure by prescribing that a rating should be made at one compression ratio higher than that producing incipient knock, which should result in a knock intensity equivalent to that obtained by a 65 per cent blend of iso-octane in 35 per cent normal heptane with the engine set a 5.3 to 1 compression ratio at a barometric pressure of 29.92 in. of mercury.¹ Since it is difficult to determine incipient detonation exactly, particularly where other noises are present, and its reproducibility is open to question, the more definite secondary specifica-

tion has in practice largely superseded the one based on incipient knock.

The results of some tests conducted by the C.F.R. Committee on the effect of knock intensity on ratings were reported by Neil Mac-Coull.⁷ For these tests the following fuels were used: a blend of benzene in reference fuel C-9, a commercial gasoline containing at least 0.7 cm³ of lead tetraethyl per gallon, and two stabilized, highly cracked gasolines from different sources. These four fuels were rated by the nineteen member laboratories of the exchange group at two compression ratios, one 0.2 of a ratio higher than standard and one 0.2 of a ratio lower than standard. Otherwise, the method used was identical with the A.S.T.M. procedure. The results obtained indicated that increasing the compression ratio increases the knock rating, but, as might be expected, the amount of increase varies with the type of fuel. Thus the maximum increase of the average ratings of all the laboratories occurred with the benzene blend and equalled 2.2 octane numbers. The minimum increase was 0.3 octane number with the commercial fuel. The two cracked fuels gave a difference of 1.1 and 1.2 octane numbers. These differences are not very great, considering that the difference in knock intensity used was appreciable, namely, that produced by a difference in compression ratio of 0.4, whereas the standard knock intensity is such that a reduction of 1 in the compression ratio would reduce the intensity to zero.

In conclusion it may be said that, through the cooperative efforts of members of both the petroleum and automotive industries, a great deal of work, of which only a small part could be taken up within the limits of this paper, has been and still is being done towards establishing a precise means of evaluating the knock characteristics of motor fuels. It is to be hoped that the many factors regarding detonation brought out as a result of this work will also aid in shedding more light on this complex phenomenon of combustion.

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Discussion

BERNARD LEWIS AND GUENTHER VON ELBE*: It should be possible to interpret the experience in the road service tests mentioned by Mr. Best by a consideration of the ignition regions and ignition lag periods of various types of fuels.

Knocking is avoided if the flame travels throughout the combustion space of the engine in a time which is shorter than the ignition lag time of the last part of the charge to burn. The ignition lag of a given fuel-air mixture is, among other factors, a function of temperature and pressure. The lower part of the accompanying figure contains typical curves of equal ignition lags in a temperature-pressure diagram (Townend). The actual position

of these curves is influenced by engine design, but some such set will be valid for a given engine. Keeping the spark timing constant and assuming constant intake pressure and mixture composition, we shall confine ourselves mainly to the variation of the temperature of the compressed unburned charge with engine speed. This relation depends on design factors. It will be assumed that the temperature increases somewhat with engine speed, as shown in the upper part of the figure. Measurements on a C.F.R. engine have shown that the temperature goes through a maximum [SEEBER: Dissertation, Breslau, 1932; see also PHILIPPOVICH: Z. Elektrochem. 42, 472 (1936)]. While we have no further

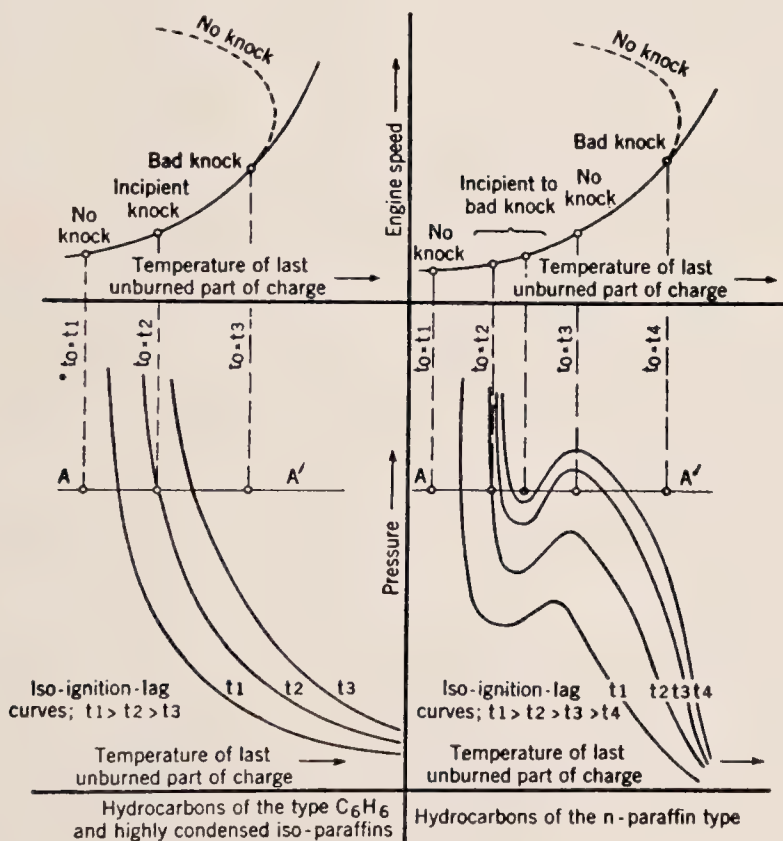


FIG. 1. Relation between knock, fuel, and engine speed.

t_s = time required for normal combustion.

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knowledge of this relation, the assumed dependence in the upper part of the figure will suffice to illustrate the possibilities of explaining the observed relationships between engine speed and knock.

Let us, for example, take the experience of service tests that a cracked fuel showed one region of knock at high speeds and a straight-run fuel two regions of knock, one at low and the other at high speeds. The behavior of the cracked fuel may be understood from the left-hand side of the figure. Let us assume that a pressure corresponding to the line AA' is reached in the last part of the charge. As the engine speed increases, the temperature increases, and the time t_0 required for normal combustion decreases (probably mainly due to turbulence). Three iso-ignition-lag curves are shown with lag periods corresponding to $t_1 > t_2 > t_3$. If $t_0 = t_1$ at the temperature shown, the flame will travel through the combustion space in a time shorter than the ignition lag and no knock will result. When, on increasing the engine speed, $t_0 = t_2$ at the temperature shown, there will be incipient knock, since the time of flame travel is just equal to the ignition lag. On further increase of the engine speed, the time required for normal combustion becomes longer than the ignition lag, the discrepancy increasing with engine speed, resulting in an increase in the severity of the knock. If the temperature-engine speed curve goes through a maximum, the knock will decrease again in severity and finally disappear. By the same procedure, it is easily seen that straight-run fuels which have the peculiar peninsula-shaped iso-ignition-lag curves shown in the right side of the figure should exhibit two knocking regions, one at low and the other at high speed.

Changes in spark timing shift the line AA' to other positions and change the position of knock with respect to engine speed accordingly, spark advance increasing the knocking tendency and spark retard decreasing it.

Although the foregoing outline is admittedly crude, it nevertheless is suggestive of the direction in which future research might move in order to find improved methods of rating fuels. The crux of the problem is the separation of pure fuel factors and

engine factors. Although the present analysis is partly hypothetical, it is not impossible that it accomplishes this separation to a satisfactory degree. It need only be assumed that the iso-ignition-lag curves are not very different in engines of the same type. This is a matter for experimental test. If this is so, then the lower part of the figure represents essentially fuel characteristics and the upper part engine characteristics. Fuel rating would then consist, in principle, in the determination of iso-ignition-lag curves. The sets of curves for two given fuels may actually cross each other. Since that fuel is better whose ignition lag curves lie farthest to the right in the figure, it is evident that fuel A may be superior to fuel B under one set of engine conditions, and inferior under another set of engine conditions. Having established the engine characteristics as is shown, for example, in the upper part of the figure, it should become possible to predict the better fuel under various service conditions.

F. L. GASTON (*Shell Petroleum Corporation, St. Louis, Missouri*): Mr. Best makes the statement that the sensitivity of a fuel does not necessarily indicate the response in knock intensity to any variable. One of the difficulties of engine research is that a change in one variable frequently causes an unavoidable change in another, and hence the various factors involved often cannot be studied one at a time.

The research method minus motor method sensitivity involves sensitivity to air intake temperature, to jacket temperature, and to speed. In some experiments which we made some time ago, the sensitivity to jacket temperature was found to be nearly twice as great as the sensitivity to intake temperature. However, raising the intake temperature reduces the weight of air drawn into the cylinder on each stroke and hence the tendency to detonation. When the results were corrected to the same volumetric efficiency, it was found that intake temperature was more effective in reducing the knock rating of temperature-sensitive fuels than a similar increase in jacket temperature, as one would expect.

MOLECULAR STRUCTURE OF HYDROCARBONS AND ENGINE KNOCK

WHEELER G. LOVELL AND JOHN M. CAMPBELL

Research Laboratories Division, General Motors Corporation, Detroit, Michigan

During the past ten years, considerable progress has been made in the development of a knowledge of the relationship between molecular structure and knocking characteristics of hydrocarbons when used as fuels in internal-combustion engines.¹⁻²² This knowledge is of considerable significance both from the engineering standpoint, where power output or thermal efficiency is a primary consideration, and also from a more theoretical standpoint, where it is desired to extend our present understanding of fuels and combustion reactions.

From the engineering standpoint, it will suffice here to point out that the efficiency of the conventional internal-combustion engine is largely dependent upon compression ratio—increasing compression ratio making possible higher efficiency and greater power output per unit of engine displacement. Thus, within certain limits, it is desirable to use a high compression ratio, but the limit to which it is possible to go is determined by the tendency of the fuel to knock. This is a very real limitation, and that it is intimately related to the subject of molecular structure is shown by the fact that the maximum power output obtainable without knock from an engine of given piston displacement may vary by as much as 50 per cent with different isomeric paraffin hydrocarbons. Needless to say, the further development of knowledge in this direction is almost certain to have an important and far-reaching influence in the engineering progress of the automobile, aviation, and petroleum-refining industries.

The unique feature of this general situation is that the still largely unknown phenomena of gaseous combustion in an engine are controlled by slight differences in the molecular structure of fuels to an extent of tremendous economic importance. We know that the structures now predominant in most commercial fuels are relatively very poor as compared with those that we would have, had we better control of chemical reactions such as those of isomerization. This situation represents a common meeting ground of molecular physics, gaseous combustion, organic chemistry, and economics of considerable social importance.

For the purposes of this symposium we are mainly concerned with what might be termed the theoretical standpoint. Certainly the observations which have thus far been made in connection with this subject provide material which can

be woven into the theory of many branches of science to give, eventually, a clearer conception of the mechanisms involved. It will be a purpose of this paper to review some of the consistent relationships between molecular structure and knock which have been found.

It now appears that chemical constitution, as revealed by molecular structure, is related to knock, and hence the ultimate utility of a fuel, in two distinct ways: first, by direct influence on knock, and second, by influencing the effectiveness of antiknock compounds when used in the fuels.

In order to evaluate the relationship between the structure of hydrocarbons and their tendency to knock, various methods have been used, all of them depending upon direct measurements in an engine. The use of an engine is essential, since we do not have precise enough information as to the conditions in an engine cylinder to enable them to be duplicated satisfactorily or conveniently outside of an engine. However, it happens that an engine under the proper conditions offers an extraordinarily sensitive, convenient, and rapid method of measurement. The development of the concept of the octane number of a fuel, and of the standardized method of its measurement, discussed in detail elsewhere in this symposium, is a specific application of this principle to the testing of commercial gasolines. This commercial testing method, because of the restricted engine conditions employed in it, is not ideally adapted to the broad study of the knocking characteristics of hydrocarbons. Consequently, in the work described herein, wide deviations from the commercial test procedure have been utilized.

One method of measurement which has been used with hydrocarbons is to burn the hydrocarbon in question as a fuel in an engine in the pure state and to determine the maximum compression ratio at which it will operate without knock. This method is quite simple and direct, although the values must, of necessity, relate to the particular engine and operating conditions used in the experiments. For some purposes this method is not entirely suitable, because the materials under test may not have physical properties adapted for use in a carburetor. It also has another disadvantage in that the use of that method of measurement requires considerable amounts of material for test, and such amounts may not always be available in the

case of compounds whose laboratory preparation is difficult.

For these and other reasons measurements have often been made in solution in a reference or standard fuel, measuring the change in knock of the fuel upon the addition to the fuel of a definite amount of the material under test. The change in knocking behavior may be conveniently expressed as the change in the equivalent octane number of the fuel or, as was done before this method came into use, it may be measured and expressed in terms of the amount of an antiknock compound such as aniline or lead tetraethyl which will produce a similar change in knocking tendency. Other modifications of these most widely used methods have been used; for a complete discussion of them and the precise methods of test and computation, reference may be made to the original papers.

As previously mentioned, all methods involve the use of an engine, and it is true that the precise values obtained will depend to an extent upon the engine used and the conditions under which it is operated. In other words, the knocking

characteristics of a fuel are not entirely a property of the fuel alone. From the limited amount of data thus far made available, it appears that, with few exceptions, the changes in the values of different hydrocarbons observed under different engine conditions are relatively small as compared with some of the differences between different hydrocarbons under comparable engine conditions. Again, for detailed expositions of these phenomena reference must be made to separate papers covering these various aspects of the subject.^{5,7,15}

It is of considerable significance, however, that under given engine conditions the knocking characteristics of hydrocarbons fall into a very consistent pattern, according to their molecular structure. The significance of this may be two-fold. This consistent behavior enables one to make an appraisal of what the possibilities are in the way of fuels whose thermodynamic efficiency in an engine may be very high, or of what efficiencies are possible when the present barriers of lack of knowledge as to chemical conversions are removed or reduced. This consistent behavior

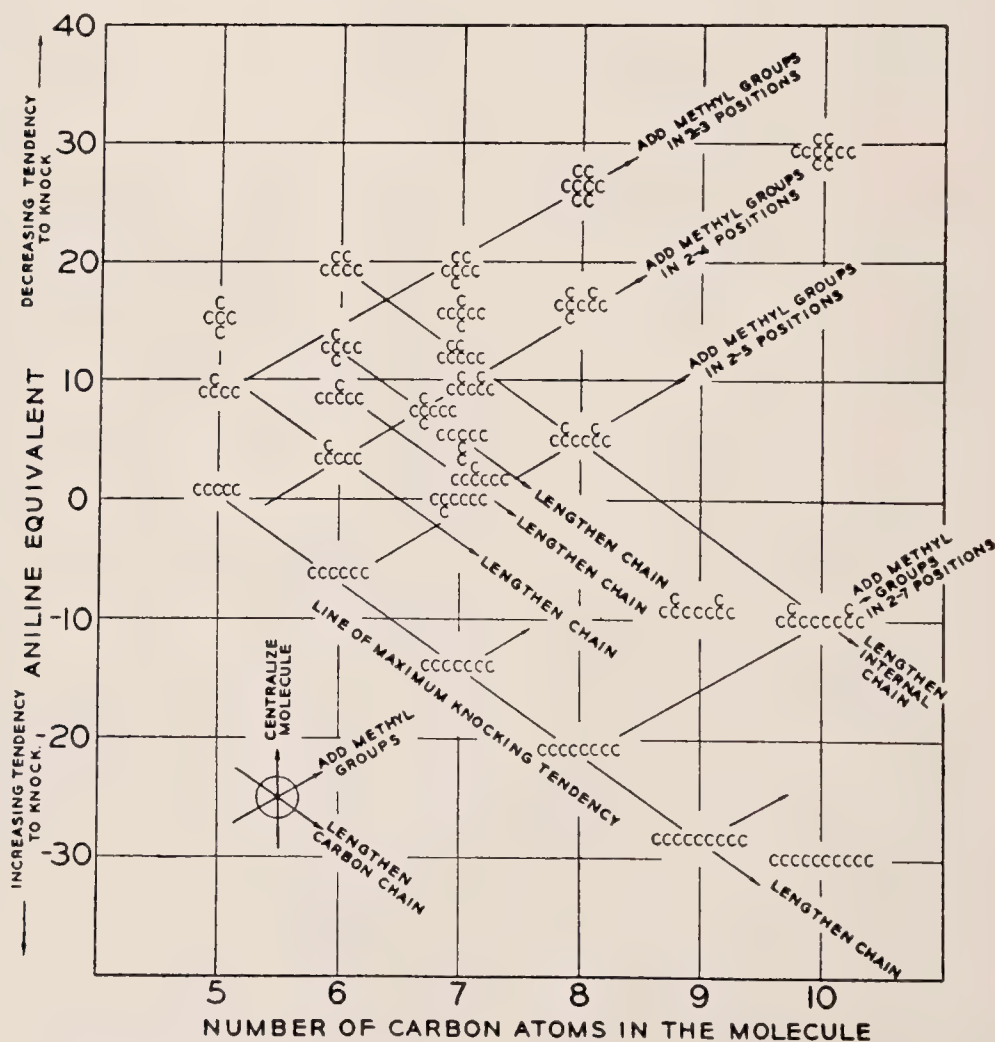


Fig. 1. Relationship of molecular structure to knocking characteristics of paraffin hydrocarbons.

may also serve as a guide in evaluating theories of the mechanism of hydrocarbon combustion and the incidence of knock in engines. For these reasons it may be valuable in a symposium of this type to review these consistencies, in order that the facts upon which theories or predictions may be based may be clearly in mind.

It is convenient for the sake of simplicity to consider the hydrocarbons in classes, such as paraffins, olefins, etc., and the relationships are most readily expressed graphically. Figure 1 summarizes the relationships for the paraffin hydrocarbons. The knocking characteristics are expressed in terms of "aniline equivalent," which is a measure of the knocking behavior in relatively dilute solution in which concentrations are on the basis of the same number of molecules.¹² In order, however, to convey some concept of the scale of aniline equivalent, it may be said that *n*-heptane with an aniline equivalent of -14 and 2,2,4-trimethylpentane, which has a value of

+16, begin to knock when burned undiluted at compression ratios of 2.7 and 6.9, respectively. While such values do not permit a direct conversion of all values, because the relative values obtained in dilute solution with gasoline are not necessarily an index to behavior in the undiluted state, nevertheless they do give an idea of the great range covered by the vertical scale.

From this diagrammatic representation it may be seen that in a very general, and consistent way the addition of methyl groups improves the molecule from a knock standpoint; lengthening the straight chain of a molecule makes the knocking characteristics worse, and centralizing the molecule, without changing the number of atoms, makes a much better molecule as far as knock is concerned. On this molecular basis it is a fair approximation to say that the knock depends roughly upon the length of the unbranched straight chain of carbon atoms in the molecule. This is a fact that is probably of con-

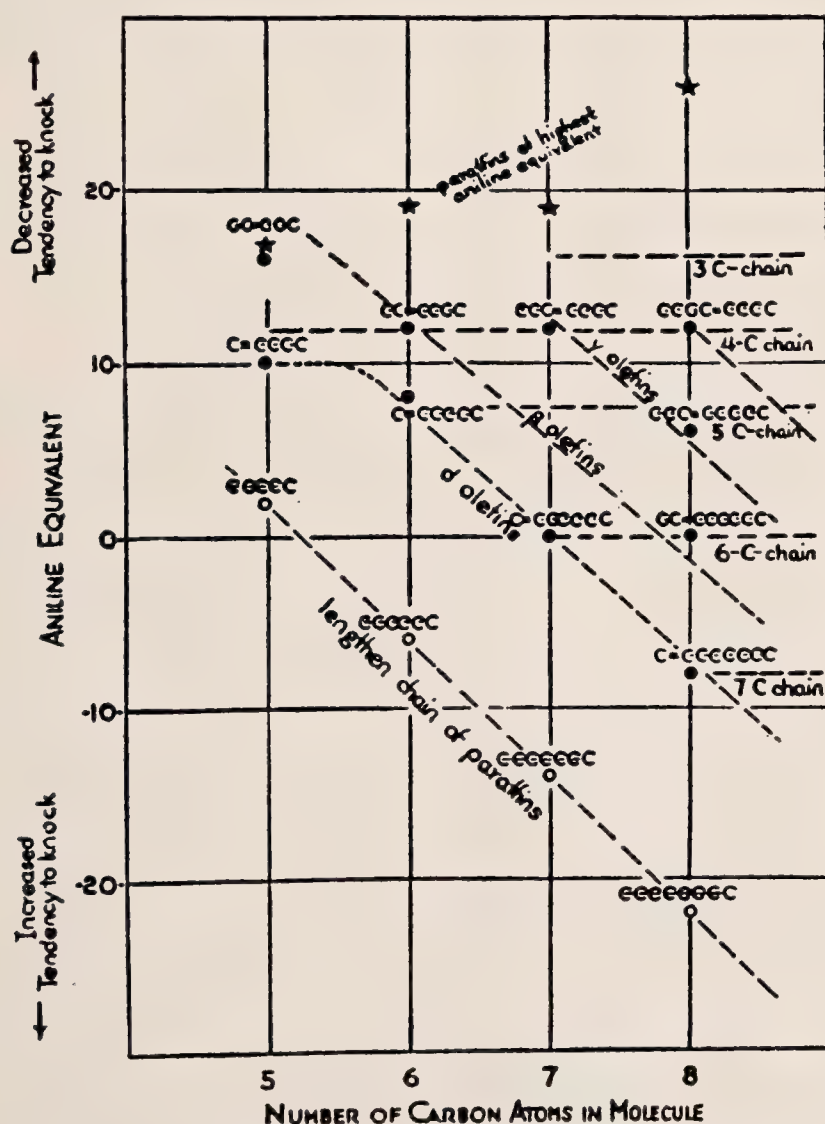


FIG. 2. Knocking characteristics of straight-chain olefins.

siderable significance as far as theories of the mechanism of combustion and knock are concerned.

This same behavior is also exhibited by the straight-chain olefin hydrocarbons, whose properties in this regard are represented graphically in Fig. 2.¹³ The effect of an increase in the straight paraffin chain is similar, both qualitatively and quantitatively, to that observed in the case of the paraffin hydrocarbons. It is also probably significant that, within the range covered, the knock seems to depend upon the length of the straight paraffin chain, irrespective of the size of the molecule.

Branched-chain olefins behave very much as might be expected from what might be termed the effect of the double bond, as revealed by the straight-chain olefins, combined with the effect of branching, as shown by the behavior of the paraffins. The great numbers of isomers of such compounds, however, make the obtaining of a

complete picture of their behavior a very difficult and tedious matter.

Another class of hydrocarbons is that of those containing a cyclopentane or a cyclohexane ring.¹⁴ In general the formation of a ring, as indicated by the behavior of cyclopentane, cyclohexane, and cycloheptane, is to enhance the degree of freedom from knock of the compound as compared with the paraffin containing the corresponding number of carbon atoms. The possibilities of isomerization in this class of compound are somewhat different from those in the aliphatic compounds, although the effect of changes in the arrangement of an alkyl side chain is similar to that which might be expected by analogy with the paraffin hydrocarbons. This is shown by the graphical representation of the data on the cyclohexanes and cyclohexenes in Fig. 3, plotted in a manner similar to the preceding data. The possibilities of isomerism due to variations in the positions of two or more side

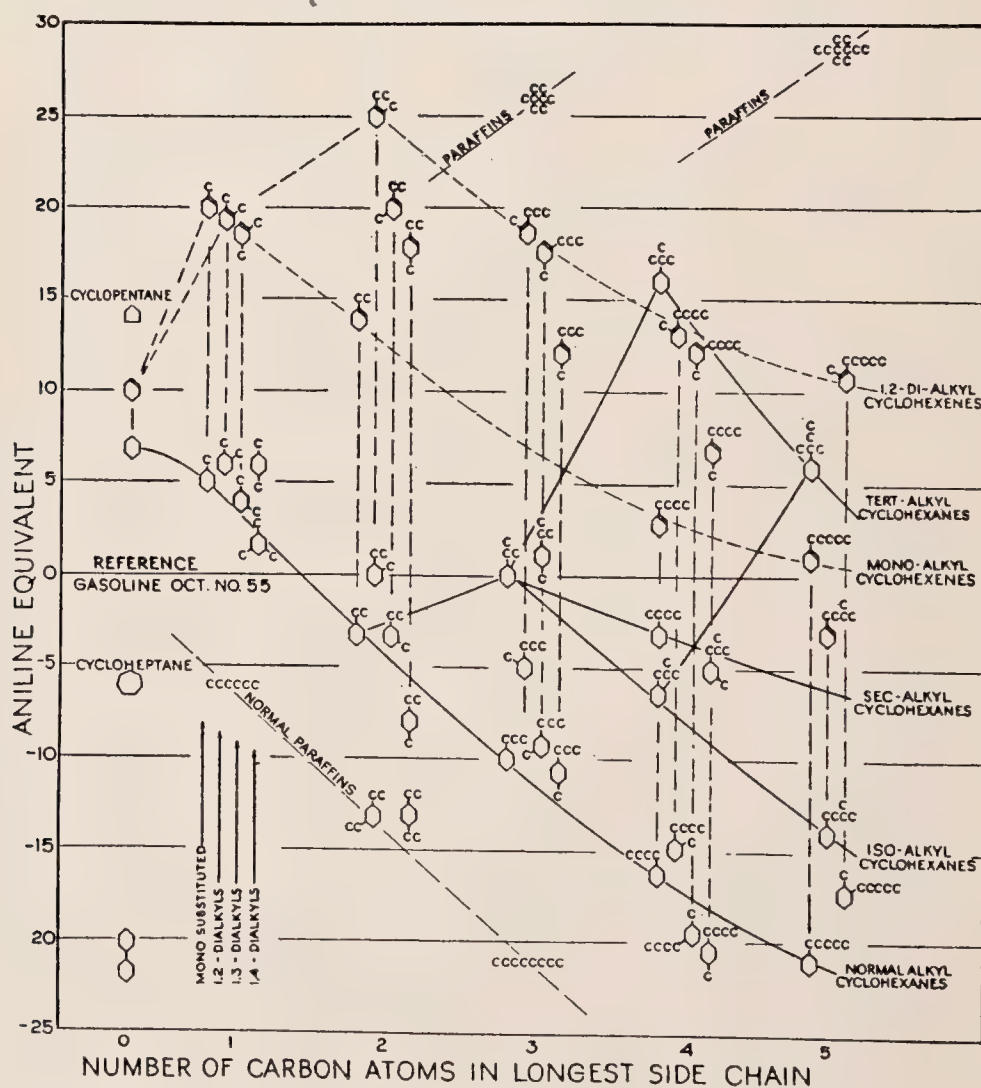


FIG. 3. Relative knocking characteristics of alkyl cyclohexanes and cyclohexenes.

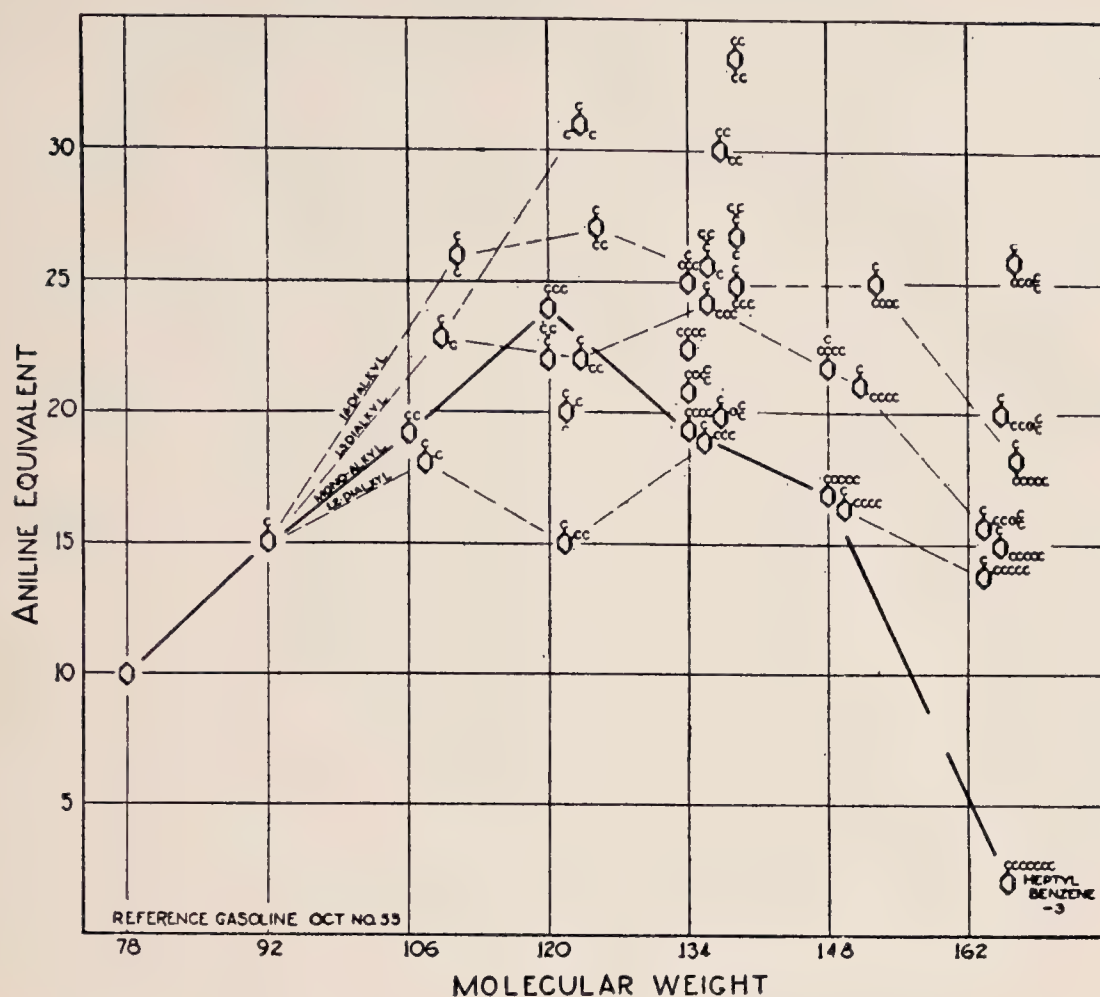


FIG. 4. Relative knocking characteristics of aromatic hydrocarbons.

chains have not seemed to be a relatively great factor in determining knock. However, the available data do seem to indicate that, as far as isomerism with respect to a different distribution of carbon atoms between chains is concerned, the most favorable condition from the standpoint of knock prevails with the most centralized structure. If we should define such a rough concept as centralization by a compact arrangement of the plane structural formula ordinarily used, this generalization seems to apply quite generally to all types of compounds investigated. It is also interesting in connection with these cyclic compounds that an introduction of a double bond in the ring increases the freedom from knock of the compound by an amount which seems quite constant.

Cyclopentanes and cyclopentenenes seem to behave, as far as their knocking characteristics are concerned, in a manner quite analogous to that of the six-membered rings.

Another class of hydrocarbons of considerable interest in connection with the problem of knock is that of the aromatic compounds containing a single benzene ring.¹⁵ Data on these are repre-

sented graphically in Fig. 4. The behavior of these compounds is different from that of the naphthenes as far as the effect of an increasing length of side chain is concerned. The addition of a side chain and its progressive lengthening first results in an increase in freedom from knock; further lengthening of the chain results in a decrease. While this peculiarity might suggest some analogy to be expected with the behavior of these compounds on oxidation, at present this is largely speculative. The effect of the initial methyl substituents, however, is very pronounced, as toluene is much better than benzene, and the xylenes and mesitylene are still better; the effect of position isomerism seems to be a large factor. The aromatic compounds behave with respect to knock as if the benzene ring were of paramount importance and as if the addition of one or more carbon atoms to it were of much greater effect than the arrangement of the atoms within the chain which is added. Most of the aromatic compounds are relatively good from the standpoint of knock as compared with the other conventional classes of hydrocarbons; it is, however, quite difficult if not impossible to assign

relative values to these classes as a whole, since the range covered by the different classes is widely, if not almost completely, overlapping.

The relationships just discussed relate to dilute solutions and are upon a molecular basis; they are of primary interest because of the suggestive consistencies of the correlations between knock and structure. From the standpoint of the fuel and the engine they are of particular interest, as indicating what may be obtained in practice from relatively small additions of different hydrocarbons in making up fuels better than those now commercially available and with a fairly wide range of constituents.

From the standpoint of making large advances in fuel technology, the knocking behavior of individual hydrocarbons in the pure state is of special importance. Considerable data are available on pure hydrocarbons in terms of the compression ratios that may be used with them, although of necessity, as previously mentioned, they are of more limited extent. The general qualitative correlations between knocking characteristics and molecular structure previously observed for such hydrocarbons when measured in dilute solutions hold in general, but there are some notable exceptions. These arise from the fact that the critical compression ratio of a mixture of two compounds is not always directly proportional to the concentration of each in the

mixture. There is also another contributing factor which will be discussed later, namely, that the engine operating conditions make a considerable difference in the relative values obtained for some fuels when they are tested in the pure state.

However, a general picture of the relationships among the paraffin hydrocarbons is shown in Fig. 5, where the knocking characteristics of the pure paraffin hydrocarbons are evaluated in terms of the critical compression ratio or the highest ratio at which they can be used without knocking.¹⁶ Most apparent, of course, are the very great differences between the different compounds.

A similar picture for the cyclic compounds is shown in Fig. 6. Outstanding here are the very great differences between the aromatic compounds and the corresponding saturated compounds, a phenomenon which does not appear with measurements made under conditions of dilute solutions. The knocking tendency of a mixture is not necessarily a linear function of the concentration. This behavior is shown by the data of Fig. 7, in which the critical compression ratio of some two-component mixtures is plotted against the mole fraction in the solution. The curves are not linear and show a wide variety of characteristics, some being convex and some concave downward. In general, extrapolation of knock-concentration curves over a considerable

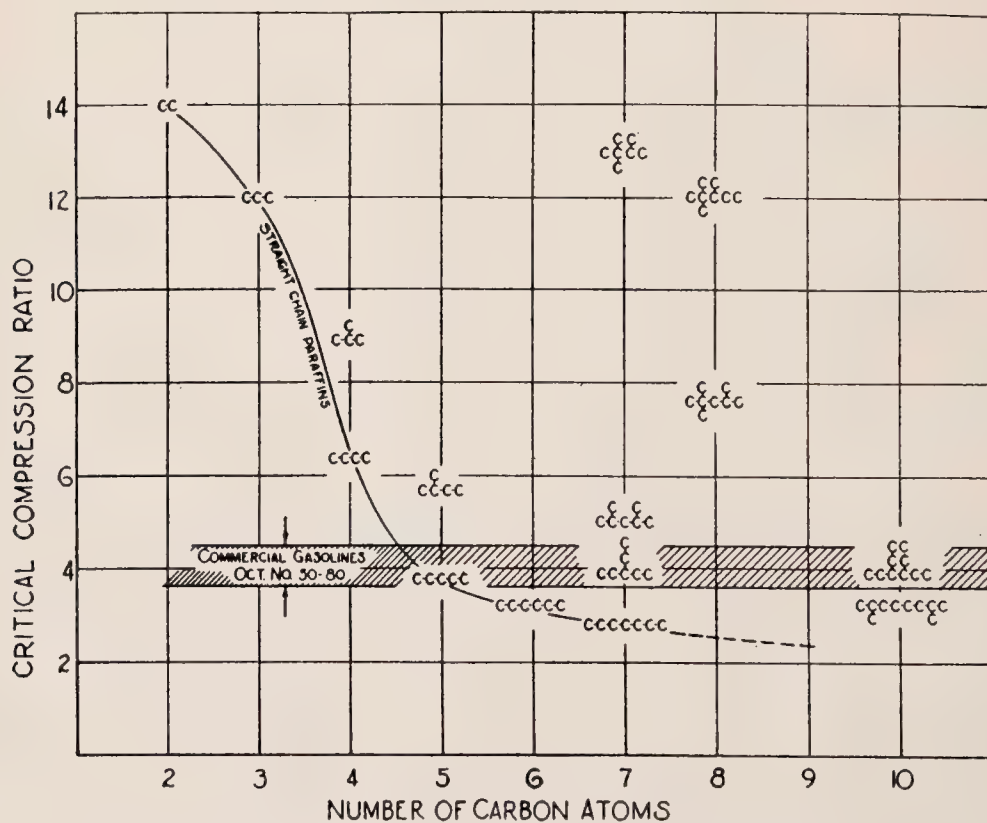


FIG. 5. Critical compression ratios of paraffin hydrocarbons.

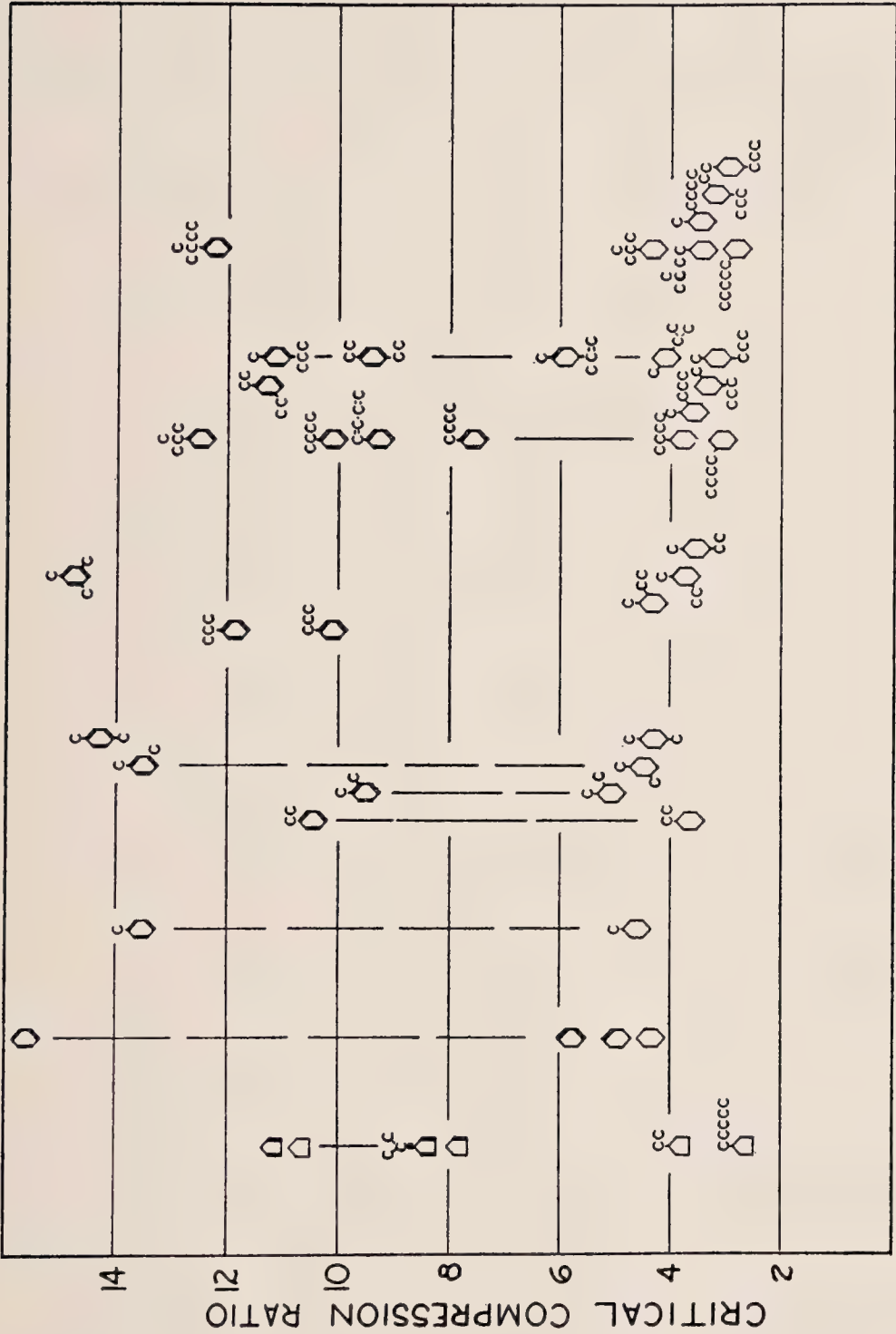


Fig. 6. Comparison of benzene and cyclohexane derivatives.

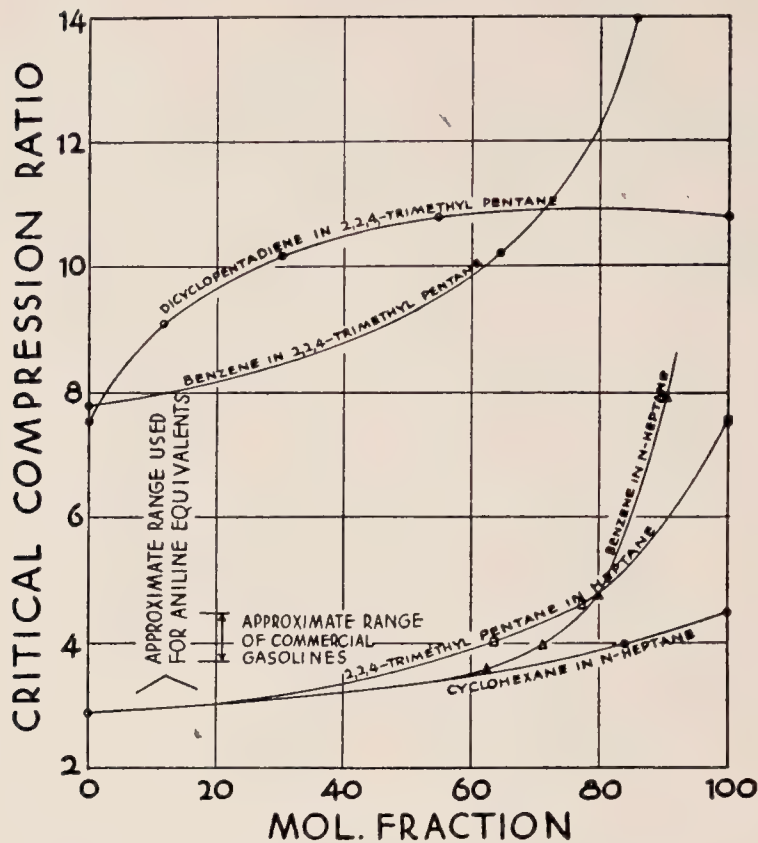


FIG. 7. Knocking characteristics of two-component hydrocarbon mixtures.

range is not justified. The reasons for these departures from mere simple relationships are of considerable speculative interest, but our present knowledge of hydrocarbon combustion is possibly

too limited to warrant extensive discussion of this here. The relationships among hydrocarbons with respect to knock and utility are also of interest

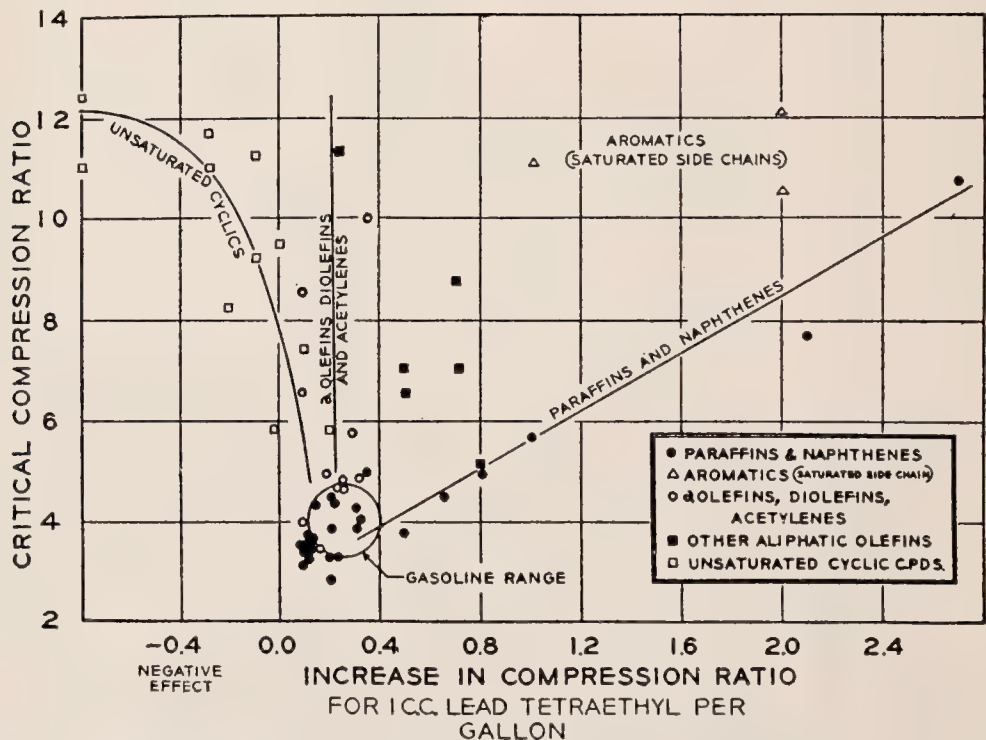


FIG. 8. Relative antiknock effect of lead tetraethyl in various types of hydrocarbons.

from the viewpoint of the mechanism of combustion, because of the way in which antiknock compounds act upon them.^{3,5,6} The mechanism of antiknock action seems to be tied up with the molecular structure of the hydrocarbon, probably as a result of the intermediate compounds formed. In some compounds lead tetraethyl, for instance, may be twenty times as effective as a knock suppressor as in others; in some compounds it may even be a knock inducer.

As an index of this effectiveness, we may consider the increase in critical compression ratio which the addition of 1 cm³ of lead tetraethyl will permit. It is possible to correlate such values upon the basis of the branching of carbon chains, upon the position of double bonds in a chain or in a ring, and so on. These manifold and consistent relationships may not well be detailed here. However, as a rough general correlation, the data shown graphically in Fig. 8 indicate the extent of the variation, since the addition of 1 cm³ of lead tetraethyl to a hydrocarbon may permit an increase of 2.7 ratios without knock, or may necessitate a decrease of 0.8 of a compression ratio. As a single example of how specific this effect is, there are the data of Fig. 9, which are self-explanatory. Since any consistent theory of knock must include the action of antiknock compounds, it is important to note that some antiknock compounds or catalysts may under some circumstances act as knock-inducing compounds.

An evaluation of the relative utilities of fuels of different molecular structures is essentially a measurement of the thermodynamic efficiency

with which each may be burned in an engine suited to that particular fuel. As mentioned previously, this is a property not entirely of the fuel but also of the engine; the engine must to a considerable extent be adapted to the fuel in other respects than simply in regard to the compression ratio.

A concept of why this comes about may be readily gained by thinking of the phenomenon of knock as essentially a race between two combustion processes in the engine cylinder. The first is the spread of flame across the cylinder; the second is the series of steps leading up to ignition of the fuel-air mixture ahead of the flame. Which phenomenon takes place first determines whether or not there is knock. Both processes are influenced by the time available, by temperature, and by pressure, so that the outcome of the race will depend upon such conditions. Furthermore, the extent to which these different processes are affected by temperature and pressure will vary from one hydrocarbon fuel to another. It is to be expected, consequently, that the attainment of the greatest efficiency is to be had only by the best fitting together of fuel and engine. This amounts to selecting a raw material (fuel) and carrying out a chemical reaction on it (combustion with air) under conditions best adapted to secure the greatest yield of work with it. The selection of the initial fuel material is influenced, first, by the relative ease with which it may be made from petroleum or other raw material, and, second, by the conditions which it requires for its best combustion.

The first factor, that of the preparation of the fuel from petroleum or other sources of raw material, is dealt with in other papers of this symposium; the conditions for best combustion may be outlined here so as to show some of the controlling conditions influencing the selection of fuels.

As is well known, the compression ratio gives a fair index of the relative thermodynamic efficiency of combustion, if and only if other factors are kept constant. The numerical values of compression ratio so obtained, however, are quite without absolute significance, except as they pertain to the particular conditions utilized. An evaluation of such a scale is Fig. 10, where, taking the data from one variable compression engine, brake mean effective pressures are plotted against the compression ratios at which the engine was operated. Spotted along the curve are a number of points which represent the highest compression ratio at which the hydrocarbons indicated may be used without knock, under the particular conditions of the tests. Three such curves are shown, representing different engine speeds and different temperatures of the cylinder jacket. It is

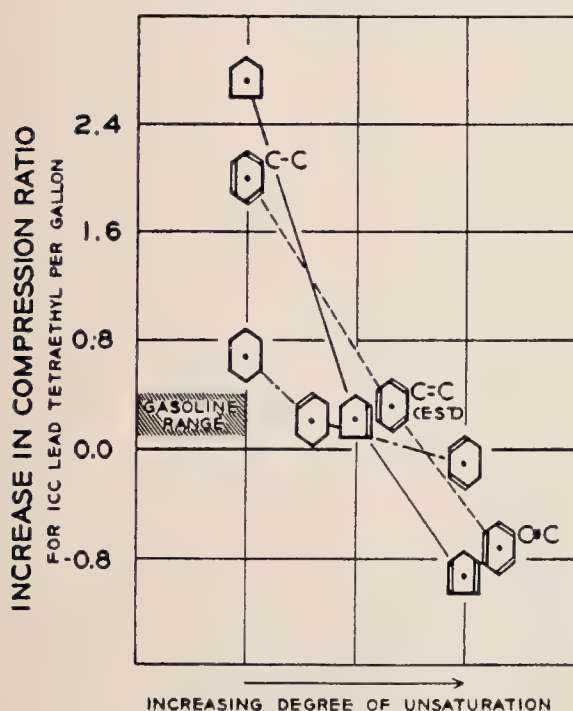


FIG. 9. Effect of double bonds in cyclic compounds on effectiveness of lead tetraethyl.

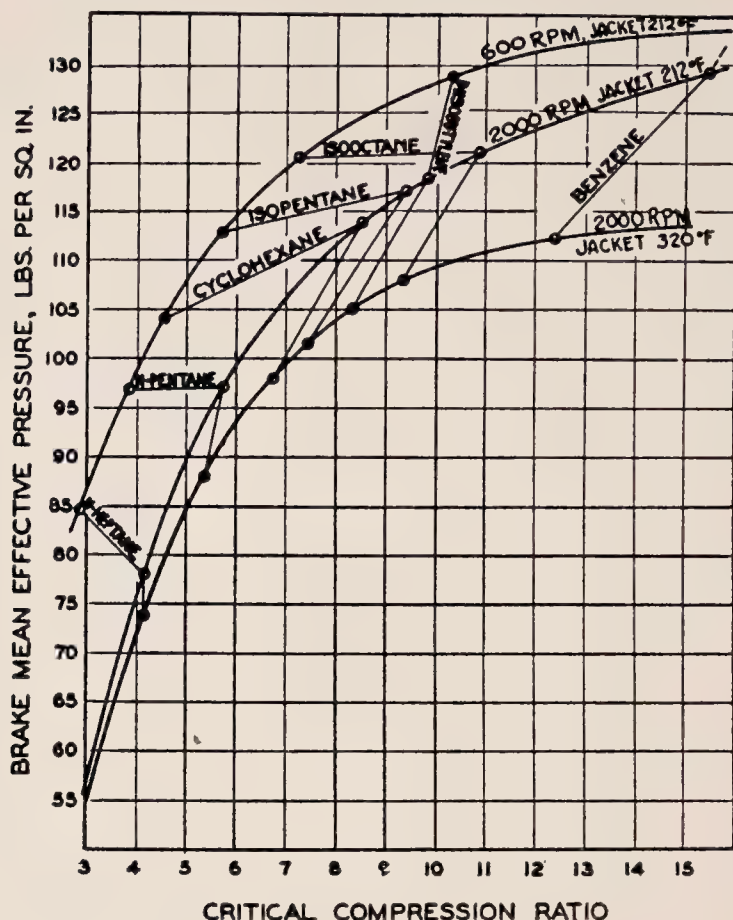


FIG. 10. Power characteristics of a $3\frac{1}{4}$ in. \times $4\frac{1}{2}$ in. single-cylinder, variable-compression engine. Mixture ratio and spark timing for maximum power. Mixture temperature approximately 60°F .

obvious from the three curves that with different fuels there are very great differences between the efficiencies or power outputs possible with knock-free operation.

Equally important are the changes in the relative behavior of different hydrocarbons when burned in an engine under different operating conditions. The paraffins and cyclohexane decreased in knocking tendency as the speed was increased, Diisobutylene, an olefin, knocked more with increasing speed, as shown by the lowering of the critical compression ratio with increased speed. Increasing the jacket temperature resulted in general in an increase in knocking tendency, although the change varied greatly from one fuel to another.

The comparison between isooctane and diisobutylene is of particular interest because it illustrates the differences in knocking characteristics, as affected by engine conditions, that may exist between an olefin and the corresponding paraffin. At 600 rpm, diisobutylene has much less tendency to knock than isooctane under the engine conditions represented in Fig. 10. But, at 2000 rpm, the relative knocking tendencies of

these two hydrocarbons are completely reversed and the saturated paraffin, isooctane (2,2,4-trimethylpentane), becomes the superior fuel.

These data indicate that the relative knocking tendencies of different hydrocarbons may be expected to be affected to a considerable degree by changes in engine conditions. Consequently the choice of fuel and engine conditions to be used for the production of maximum output involves an evaluation of the relative effects of a number of different variables, of which only two of the more outstanding ones—engine speed and jacket temperature—have been discussed herein.

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